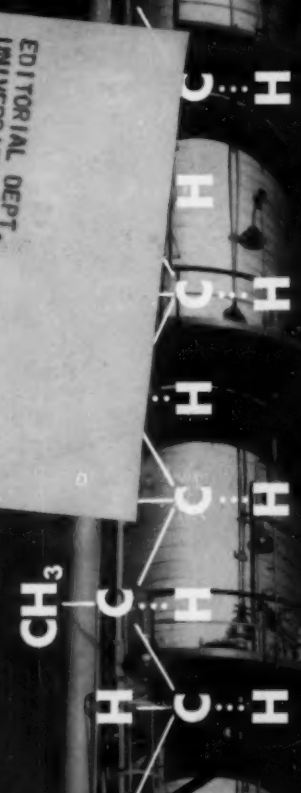
SPE JOURNAL

The Official Publication of the Society of Plastics Engineers, Inc.

POLYPROPYLENE

- Physical Properties
- Processing

— Page 1039



EDITORIAL DEPT.
UNIVERSITY MICROFILMS, INC.
313 N. FIRST ST.
ANN ARBOR, MICH.

VOL. 16, NO. 9 • SEPTEMBER 1960

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BRIEFS

SALES SERVICE LABORATORY **REPORT 60-3**

MOLDING MARLEX*, A New Publication

Our new bi-monthly newsletter has on its masthead this statement: "published for all skilled craftsmen devoted to the art of injection molding." As advertised, it's intended primarily for those fellows doing the actual molding . . . plant managers, shop foremen, and machine operators. However, we feel it should interest almost everyone in the business. The March-April and May-June issues have already been distributed. If you didn't get them, let us know, and we'll put you on the list—sending you these past issues if we can. From those who have seen MOLDING MARLEX, we are open to comments, criticisms, suggestions—anything to make forthcoming issues more interesting and useful.

Wire and Cable— Onward Extrusion!

Just recently, when we mentioned the new MARLEX tailored resins, TR-201 and TR-202, to a wire-and-cable friend . . . he groaned. "Oh no—not another one!" Unknowingly, he hit it right on the head. These new MARLEX resins—specially tailored for wire and cable coating—are not *just other plastic insulations*. Once he had examined the data, our friend was impressed. "Who knows," he mumbled, "these new MARLEX resins may even sell extrusion to the old timers who think that the only way to put on quality insulation is with strip vulcanization and that secret formulation mixed in 'ye ole Banbury'!"

What makes TR-201 and TR-202 so good? In a nutshell: (1) low dielectric constant and loss factor over a wide frequency range (essentially unaffected by climate or temporary overloads); (2) stabilization against thermal degradation as well as protection against oxidation and ozone deterioration; (3) excellent processing characteristics that, among other things, assure fast extrusion rates, uniform insulation thickness, and complete adhesion to the conductor; and (4) outstanding toughness, stress-cracking resistance, and durability. Good dielectric properties and toughness are inherent with MARLEX high density plastics. The other characteristics, which make TR-201 and TR-202 so suited for wire and cable, are obtained by tailoring a low melt resin.

To date, MARLEX TR-201 and TR-202 (the latter for thin coatings and small wire) have been used on wire ranging from #14 to #3/0 . . . and as insulation and jackets on regular and armored, multi-conductor cables. In addition to thousands of lab tests, we've installed about 40,000 feet of MARLEX insulated and jacketed lines in a variety of situations—direct burial and aerial for utility distribution, cathodic protection, etc. Regular splicing techniques and materials were used. Early evaluation of these installations is verifying the wonderful performance lab tests indicated we could expect. If you'll write, we will fill you in on the technical details.

Pipe and Conduit . . . anyone for Quality?

We are encouraged these days by the growing insistence on rigid resin specifications for pipe and conduit. It's only natural, since we sell high quality, virgin material for these applications—developed, we might add, at considerable expense. The growing acceptance of electrical conduit, engineered and coilable pipe made from MARLEX TR-212 and TR-213 by municipalities and utilities is responsible for the trend. You can't satisfy these "pros" with off-grade stuff, scraps, and a little carbon black—no matter how good the finished extrusion looks. They require that extruders meet specifications for tensile and rupture strength, flexure, thermal range, dielectric, hardness, NSF approval, etc.

The demand for quality, high density, plastic pipe and conduit is mushrooming . . . and the potential is enormous. For those extruders who want to jump on the bandwagon, we've lined up a real program—complete with production, marketing, and promotion assistance. Write or call us up and we'll arrange to show you the whole works. You'll be impressed!

*MARLEX is a trademark for Phillips family of olefin polymers.

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SPE JOURNAL

plastics engineering trends of technical *significance*

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SPE Journal Newsletter ____ 1005

Special Feature—Multiple Level Injection Molding
Ernest J. Csaszar, Newark Die Co., and Theodore Saulino, Royal Associates
A method for doubling the number of cavities in a given clamping area ____ 1009

Regional Technical Conference—Plastics versus Corrosion
Golden Gate Section of SPE sponsors RETEC ____ 1018

SPE Journal Features

Speaking of Extrusion—Flow Patterns in a Single Screw Extruder
W. D. Mohr, P. H. Squires, and F. C. Starr, Du Pont Co.
Photographs of flow in channel show patterns visually ____ 1015

Molding Cycles—Mold Fill Time Considerations
Gordon B. Thayer, Dow Chemical Co.
Colder mold walls can result in faster molding cycles ____ 1021

Reinforced Plastics—A Glossary of Terms
Arthur Smith, Rohm and Haas Co.
Nomenclature and terms used in processing and research ____ 1024

Polymer Science—Energies of Polymer Decomposition, Part II
Leo A. Wall, National Bureau of Standards
Condensed phase studies offers promising method for determining dissociation energies of polymer bonds ____ 1031

Technical Articles

☐ **Physical Properties and Processing of Polypropylene**
W. L. Dunkel and R. A. Westlund, Jr., Enjay Chemical Co.
How certain physical properties affect processing characteristics ____ 1039

☐ **Porous Plastic Laminates**
James T. Hill, Egbert de Vries, and Fred Leonard, U.S. Army Prosthetics Research Laboratory, Walter Reed Army Medical Center
A method for preparing void-free, complex shaped resin-fabric laminates ____ 1047

☐ **Coloring Linear Polyethylene**
P. E. Campbell, R. J. Martinovich, and T. V. Gay, Phillips Chemical Co.
Article gives three screening tests for pigments ____ 1052

☐ **Roll Leaf Stamping—Ideas for Finishing**
Martin A. Olsen, OlsenMark Corp.
Design, molding tips, and formulation possibilities ____ 1056

News of The Society

Society Action—SPE's Public Relations Program Now Rolling
Frederick C. Sutro, Jr., Chairman, Public Relations Committee ____ 1059

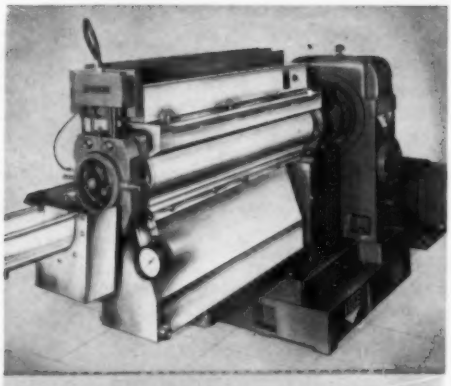
PAG Progress—Finishing PAG Blueprints Pattern for Successful Workshops
T. E. Hayden, Chairman, Finishing PAG ____ 1062

Departments

Editorial ____ 1001
Technical Meetings Calendar ____ 1073
Section News ____ 1074
About Members ____ 1075
Plastics Around the World ____ 1066
New Books ____ 1064
Employment and Service Guide ____ 1076
Advertisers' Index ____ 1078

The Cover

The Humble Oil and Refining Company's new polypropylene plant at Baytown, Texas, shown on the cover, produces polymer via a continuous process. Article on page 1039 shows how physical properties of this polymer affect processing characteristics.



#3 (3½" bore) Royle Spirod Extruder showing section of retractable Cooling Tank.

for plastic pipe production specify ROYLE right down the line!

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The new Royle Dual Coiler developed to coil flexible pipe or tubing. It features collapsible coiling heads, electric clutches for engaging heads, prewired operator's control station and constant torque drive.

If you produce plastic pipe — polyethylene, rigid or semi-rigid PVC, Kralastic, Cycolac, nylon, polypropylene or any other compound —choose Royle equipment.

Now you can get Royle quality — Royle dependability — Royle performance along your entire pipe production line — from hopper to finished plastic pipe. Every unit you need can carry the famous Royle triangle — Extruders, Cooling Tanks, Pipe Haul-Offs and Coilers; as well as all necessary auxiliary equipment, including Control Panels, Dies and Cutting equipment.

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CYMEL 3135 – 3136 (glass-filled) Additional distinctive properties: outstanding electrical properties; high impact resistance; extraordinary flame resistance; good dimensional stability. Typical applications: circuit breaker boxes; terminal strips; connectors; coil forms; stand-off insulators. Specifications: Cymel 3135 (MMI-30, MIL-M-14E, Federal L-M-181 Type 8; ASTM D704-55T Type 8); Cymel 3136 (MIL-M-19061, MMI-5).

CYMEL 592 (asbestos-filled) Additional distinctive properties: resistance to atmospheric extremes; high dielectric strength. Typical applications: connector plugs; terminal blocks; a/c, automotive and heavy duty industrial ignition parts. Specifications: MIL-M-14E MME; Federal L-M-181 Type 2; ASTM D704-55T Type 2, SPI SPEC NO. 27025.

CYMEL 1077 (alpha cellulose-filled) Additional distinctive properties: Surface hardness, heat resistance, unlimited color range. Typical applications: appliance housings, shaver housings, business machine keys. Specifications: MIL-M-14E – Type CMG (in approved colors); Federal L-M-181 Type 1; ASTM D704-55T Type 1, SPI SPEC NO. 30026.

CYMEL 1500 (wood flour-filled) – CYMEL 1502 (alpha cellulose-filled) Additional distinctive properties: Good insert retention. Typical applications: meter blocks, ignition parts, terminal strips. Specifications: Cymel 1500 (MIL-M-14E Type CMG, Federal L-M-181 Type 6, ASTM D704-55T Type 6); Cymel 1502 (MIL-M-14E Type CMG, Federal L-M-181 Type 7; ASTM D704-55T Type 7.

BEETLE® UREA (alpha-filled) Additional distinctive properties: Economy of fabrication, economy of material, myriad translucent and opaque colors. Typical applications: wiring devices, home circuit breakers, tube bases, appliance housings. Specifications: Federal L-P-406A, LC 726-1, ASTM D705-55, Grade 1 (Arc resistance limits are in process of revision by ASTM), SPI SPEC NO. 27026.

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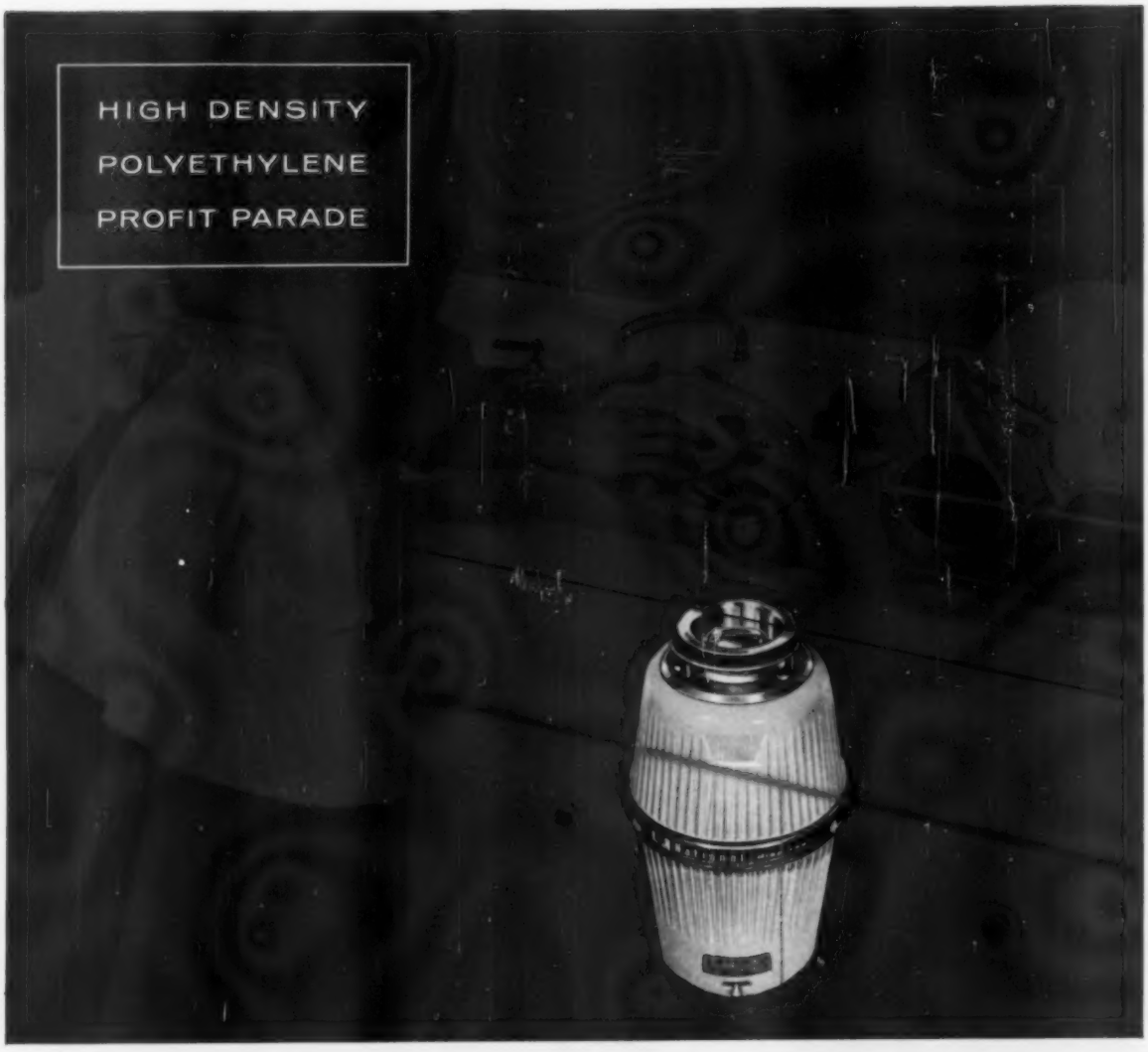


Grace Plastic Upgrades New Appliance Model

The new Citation Model National Disposer shows how the use of Grex high density polyethylene results in upgrading a product to increase its consumer appeal.

Made by the Plumbing Equipment Division of National Rubber Machinery Company, the appliance grinds food wastes into micro-sized particles that wash down the drain. Its primary appeal is freedom from garbage-handling chores. Three additional sales-stimulating features are direct results of specifying Grex for the housing:

1. Freedom of design due to the moldability of the Grace plastic provides clean, fresh styling.

2. A choice of attractive colors is offered. Colors are molded into the Grex housing—can't peel, chip or fade.

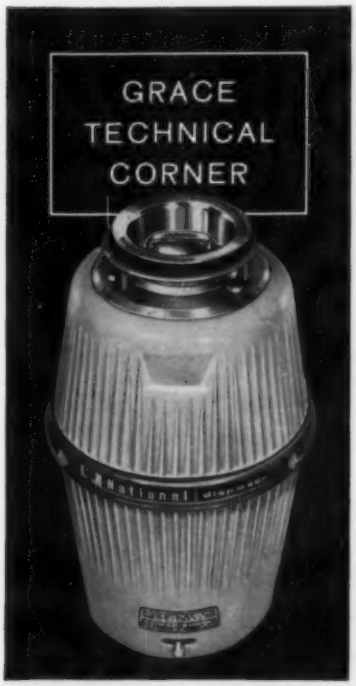
3. The plastic's sound-deadening properties are utilized to help make the Disposer operate "whisper quiet."

In addition to these features, the housing is strong, rigid and virtually indestructible. It cannot rust, is unaffected by chemicals normally corrosive to other materials and withstands the high temperature of boiling water.

If you are looking for ways to upgrade your product it will pay you to find out exactly what high density polyethylene has to offer by calling in the experts. Grace has the production, technical, and marketing facilities to help put your product in the Grex profit parade. Everyone says we're easy to do business with.

Grex is the trademark for W. R. Grace & Co.'s Polyolefins.

W.R. GRACE & CO.
POLYMER CHEMICALS DIVISION CLIFTON, NEW JERSEY



What are the advantages of using Grex to make a product prototype?

The prototype for the new model National Food Waste Disposer shown here was vacuum formed from Grex sheet in our Clifton Laboratories. Whenever possible, prototypes of products designed for production with high density polyethylene should be made of the same material. This is the best way to see how the product will look and feel before costly molds are built and production actually started.

Helpful in marketing. Although most prototypes are required from an engineering standpoint they are often useful to guide marketing decisions as well. This was the case with the Grex prototype of the National Disposer. The object was to determine, in advance of production, how the trade would react to the new model by presenting prototypes or samples that come as close as possible to the finished product.

Grace's part. Working from the manufacturer's engineering drawings Grace designed wooden molds and vacuum formed a number of samples from Grex sheet. The samples were sent to the manufacturer for finishing (trimming of flash and drilling the necessary holes), and returned to Clifton for surface finishing. The samples were completed in time for display at an important trade show. Trade reaction was highly favorable, just as you would expect from reading about the product on the opposite page.

You are invited to take advantage of Grace technical service. Perhaps we can help you by making a Grex prototype for your high density polyethylene application. Or perhaps you need assistance on other aspects of design or production of high density polyethylene parts. If so, now is the time to contact:

Technical Service Department
W. R. Grace & Co., Clifton, New Jersey

EDITORIAL

The Personal Responsibilities of Keeping Technical Knowledge Current

Great efforts are being made to make easier the reading this industry's research scientists, engineers, executives should do. Data and articles appear in all sorts of capsules, briefs, and telegraphic forms. But two basic tenets must not be forgotten in this fetish for conserving time and effort:

1. There is no substitute for reading and study if one is to keep his store of technical knowledge current.

2. There is no substitute for reading the author's original and complete technical article. No matter how skillfully an article is abstracted or digested, something of value is always lost in the process.

Because of the grand scale on which manufacturing and research is carried on in the plastics industry today, many believe that association with the organization relieves them of the personal responsibility of keeping their degree or diploma as up-to-date as when it was first granted. Nothing could be further from the truth. It is the indisputable obligation of every professional to be creative in his job. And reading is one important way that creative insight can be gained.

Aside from incidental benefits of creativity which reading can bring, is the ever-present possibility of uncovering signposts of new discoveries. Several years ago Prof. Giulio Natta wrote: "The molecules of these polymers [crystalline polymers of alpha-olefins] have a very regular structure with a strictly head-to-tail linkage of monomer units and contain, at least, for the long parts of the main chain, series of tertiary carbon atoms having the same stearic configuration." This was polypropylene. The history of the discovery of atomic fission is a classic example of scientists taking time to read technical journals and examine evidence built up over many years, then finally coming to the inescapable conclusion which contradicted all previous experience of nuclear physics. Countless future breakthroughs will be sparked by reading as they have in the past.

There are other academic controversies in the field of polymer research today, which when resolved, will have tremendous benefits, yet unknown, on polymer processing. For instance, the effect of hydrostatic pressure on melt rheology is currently being debated in the literature. Only by ***reading*** and after careful reflection of the facts read, will more light eventually be emitted to solve the problem for the benefit of everyone associated with the plastics industry—from the research scientist to the processor.

NOW 3 MELT INDEXES

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For the first time, polypropylene is available in three melt indexes. Now, the flow characteristics of Escon may be matched against individual processing requirements. **LOW FLOW**, low flash for high speed operations at high pressures and temperatures . . . ideal for small precision molded parts. **INTERMEDIATE FLOW**...excellent processability for most high speed molding operations at conventional pressures and temperatures. **HIGH FLOW** for rapid filling of intricate molds under high speed conditions. For complete technical information, contact the nearest Enjay office. *Home Office:* 15 West 51st Street, New York 19, N.Y. *Other Offices:* Akron • Boston • Charlotte Chicago • Detroit • Houston Los Angeles • New Orleans Plainfield, N. J. • Tulsa

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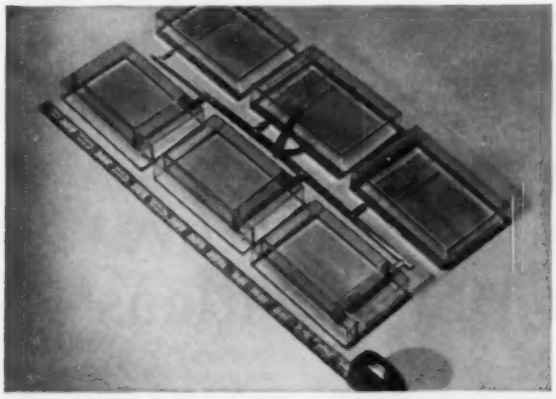
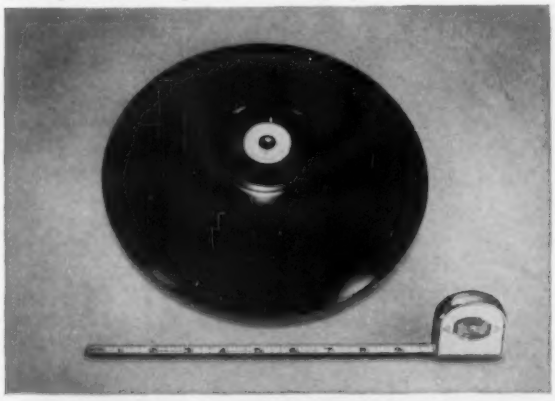
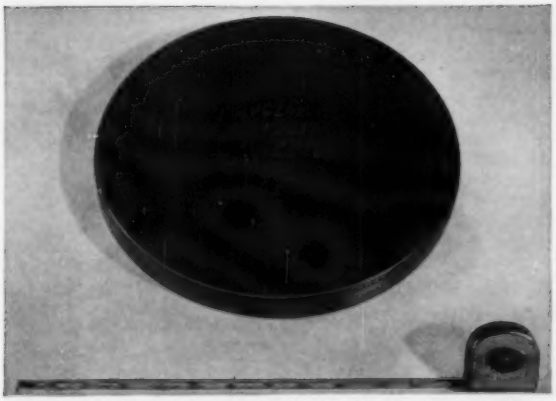
6-cavity box mold by North Star Industries, Minneapolis. Polystyrene shot weighs 6 oz. over a projected area of 90 sq. in.

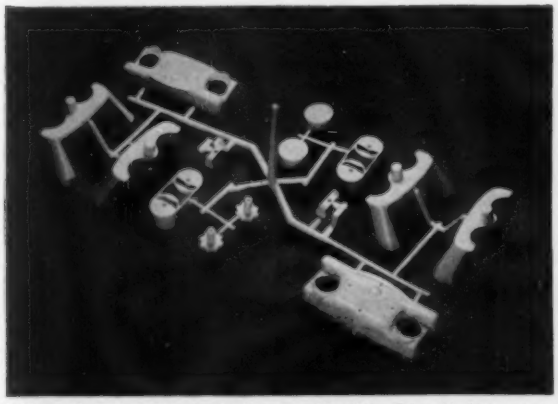


4-oz. Polystyrene Ice Bucket Lid is molded by Air Light Products, Omaha, Nebraska. Projected area is 78½ sq. in.





6-oz. Polyethylene Lid also molded by North Star Industries. Projected area of this 12" lid is 113 sq. in.



6.35-oz shot of rigid polyethylene produced by Trimold, Inc., on a 36-second cycle, molded for Fisher-Price Toys, Inc.

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4 proved stabilizers to improve your vinyl flooring formulations

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- **Elimination of sulfide staining**
- **Good light stability**
- **No lubricity**
- **High resistance to warping**

Now meet the new members of the family: Temex 3A, Temex 4 and Temex 5. Their characteristics are much the same, but each does some *specific* job particularly well . . .

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SPE JOURNAL NEWSLETTER

reading time
1 minute

Improved Reinforced Plastics

Methyl acrylate (MA) may have possibilities as a modifier for polyester resins used in making glass-reinforced laminates. Laminates made with the modified resin have good light stability, weather resistance, and moderate strength. Translucent panel industry would stand to benefit most from the advantages gained using MA.

X-Ray Plastics?

Considerable research is being done in England on the value of X-rays for detecting defects in welded plastics. Up until the present, the technique has been used for inspecting plastic welded components for telecommunications applications. However, work is now going on to apply the technique to other branches of the plastics industry. Eventual goal: To produce X-ray quality plastics to compete with X-ray quality metals.

Coating Adhesion Measured

An instrument for measuring coating adhesion by formation of blisters has been recently developed. It is based on the principle of injecting a liquid between the coating and base metal in such a way that the coating is detached in the form of oblong blisters. Pressure and volume of the injected liquid are measured and used to compute the work needed to detach the film—a measure of its adhesion.

Novel Resin Mixture

A new coating made by mixing liquefied polyethylene or polypropylene with urethanes results in a new molecular structure. Unique properties of the new resin: Stable in liquid form, good acid resistance, and improved dielectric qualities.

Plastics in Buildings

A recent report released by the Manufacturing Chemists Association (MCA) indicates that the use of plastics could be much greater than it is today. Steps are now being taken in just that direction. The Plastics in Buildings Professional Activity Group (PAG) of SPE has almost completed plans for a non-profit traveling, educational and technical exhibit of outstanding examples of plastics in buildings scheduled to get underway in April 1961 in Springfield, Mass.

STATUS REPORT:

Monsanto plastics for packaging & the food additives amendment

As part of Monsanto's continuing responsibility to customers and to package users, we present this up-to-the-minute status report of Monsanto plastics for food packaging and a brief definition of terms important to a general understanding of the Food Additives Amendment, which became effective March 6, 1960 ■ Monsanto's extensive research and development over the years have resulted in many plastic formulations from ingredients which are generally recognized as safe or which have prior sanction or which have no reasonable expectation of migration ■ By using the Monsanto plastics listed on the following page, you can be certain of packaging materials which comply with the Food Additives Amendment. We will keep you informed of additions.

Monsanto

MONSANTO DEVELOPER IN PLASTICS

The Status of Monsanto Plastics—September, 1960

PRODUCTS	BASIS FOR RECOMMENDED USE IN FOOD PACKAGING
LUSTREX® STYRENE PLASTIC	
General Purpose Molding Grades	
Hi-Flow 55 Hi-Flow 66 Hi-Flow 77	Generally recognized as safe and prior sanction.
Impact Molding and Extrusion Grades	
Hi-Test 42 Hi-Test 48 Hi-Test 88 Hi-Test 180	Extension granted by FDA until March 5, 1961 (Long term feeding studies highly favorable)
MONSANTO POLYETHYLENE (NATURAL)	
Injection and Blow Molding Grades: 51, 52, 60, 80, 705, 805, 935, 9752	Prior sanction for non-fatty foods.
Film Extrusion Grades: 30, 31, 32, 33, 34, 37, 38, 706, 10406, 13406, 18300, 19706, 23406, 25706, 26706	Extension granted by FDA until March 5, 1961. (FDA is expected to acknowledge the safety of Polyethylene in contact with fatty foods prior to this date.)
Extrusion Coating Grades: 406, 537, 73	
VUEPAK® F CELLULOSE ACETATE	Generally recognized as safe and prior sanction.
OPALON® RESINS	
300 330 FM 300 FM	Prior sanction.
Polyvinyl chloride acetate copolymers	
506 510	Prior sanction.

DEFINITIONS

of terms important in understanding the Food Additives Amendment.

Food Additives Amendment—1958 Amendment to the 1938 Federal Food, Drug and Cosmetic Act. It requires, for the first time, that any chemical compound in food, whether intentional or incidental, must be proved safe before the food is put into interstate commerce. The amendment became effective March 6, 1960.

Food Additives—All chemical compounds in food are *not*, however, in *legal* sense food additives. Compounds with prior sanction or which are generally recognized as safe are specifically excluded by the new statute from the category of food additives.

Prior Sanction—Before the 9/6/58 enactment of the Food Additives Amendment, the Food and Drug Administration and divisions of the United States Department of Agriculture had only limited authority to approve use of chemical compounds in foods. Favorable response to a request for approval normally meant an informal letter of no objection—now classified as a prior sanction—exempt under the new amendment.

Generally Recognized as Safe—The FDA interprets this to mean that it is the widely held opinion of acknowledged authorities that a given chemical compound is safe in human food. FDA has published in the Federal Register, lists of compounds which are considered generally recognized as safe.

No Reasonable Expectation of Migration—It is obvious that chemical compounds not in food cannot be food additives. But the definition of "zero" content requires scientific judgment. No reasonable expectation of migration (of pharmacological significance) realistically recognizes that infinitesimally small amounts of certain chemical compounds may be and generally are present in processed foods without hazard.

* * *

A special report on food packaging colorants has been prepared for package manufacturers using colorants in their packages. For this report, write to Monsanto Chemical Company, Plastics Division, Room 773, Springfield 2, Massachusetts.

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SPECIAL FEATURE

Multiple Level Injection Molding

E. J. Csaszar
Sales Manager, Newark Die Company

and

T. Saulino
Vice President, Royal Associates

A new and novel system of injection molding which permits doubling of cavities in a given clamping area. Key feature in the development is two levels of molding occurring at the same time with the same cycle.

Lower cost injection molding operations are the most sought-after elements of consideration in today's competitive market. Advances in present day technology of injection molding-coupled with foreign imports of finished molded items, have made it necessary for injection molders to study and otherwise investigate methods of increasing production without any increase in labor or capital investment.

One of the ways of lowering costs of molded items is to make full use of the available plasticizing capacity of an injection molding machine. The many variables that effect the overall cycle are not the subject of this discussion. However, there are certain areas of injection molding, when the geometry of the part molded uses all the apparent platen area much before the limit of plasticizing capacity of the press is reached. It is towards this segment of injection molding that multiple level injection molding has direct application.

It is not normally feasible to go beyond the press platen area with additional cavities even though the light weight of the part would indicate otherwise sufficient press capacity. For instance, there is often the problem of designing a mold where the shot weight is but 6 oz., yet the projected area would require the platen area of a 12 oz., press.

To be even more explicit, study a specific example of this condition. Consider that the job is to mold a lid for a container. This item is shallow, thin walled, and a very large projected area in proportion to its weight. For purposes of this discussion, further suppose that 4 cavities of this item would present a projected area of 80 square inches while its shot weight would be about 4 oz. Selection of a press with sufficient clamping pressure for this projected area would give considerable excess plasticizing capacity that could supply 4 more cavities, if there was more platen area and clamping pressure available. *The question is, how can we get 8 cavities into the same clamping area suitable for only 4 cavities? The answer: Two levels of molding occurring simultaneously within the same cycle.*

A novel method of performing this function is illustrated in the schematic drawing, showing a cross-section view of a typical mold incorporating the basic principles of multiple-level injection molding.

Here is a typical operation: (see diagram on page 1010) The molding material is introduced into the mold at point "A" where the press nozzle engages the sprue bushing of the mold. The material flows through the sprue bushing, thence through the auxiliary sprue bushing, branching off at points "B" and "C" to levels "X" and "Y" respectively. Then through the running system on each of these

Here are some examples of end use items which might well be molded on a two-level set-up

- Coat hangers
- Forks, spoons, platters, trays, and housewares
- Shallow containers and covers
- Fitments and aerosol caps
- Various toys
- Grilles and louvres
- Picture frames, license plate frames, etc.

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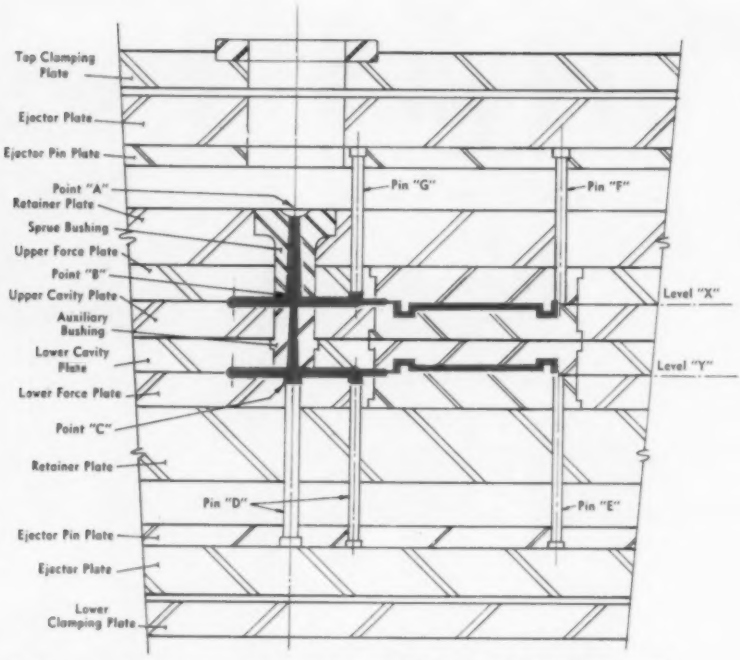


Mold and platen arrangement for multiple-level injection molding set-up. Note two levels—X and Y, each containing 4 cavities.

two levels, the material ultimately reaches the parts to be molded. After the curing portion of the cycle is completed, the press starts to open. By means of certain mechanisms, the mold opens first at level "X" causing the sprue to break away from the nozzle at point "A". Further opening of the press, parts the mold at level "Y" rupturing the auxiliary sprue at point "B". As the mold opening cycle continues, sufficient space accumulates at levels "X" and "Y" to allow for ejection of parts. The ejection of the molded parts is accomplished through the action of K/O pins "F" in the upper half of the mold and K/O pins "E" in the lower half. Simultaneously, K/O pin "D" ejects the sprue and runner from level "Y" while K/O pins "G" do the same on level "X". Inasmuch as levels "X" and "Y" are one on top of the other, the same clamping pressure that holds level "X" together acts at the same time to hold level "Y" together. The additional area represented by the second level *does not* require any additional clamping pressure. Thus, the effective platen area of the press has been doubled without the need for more clamping pressure.

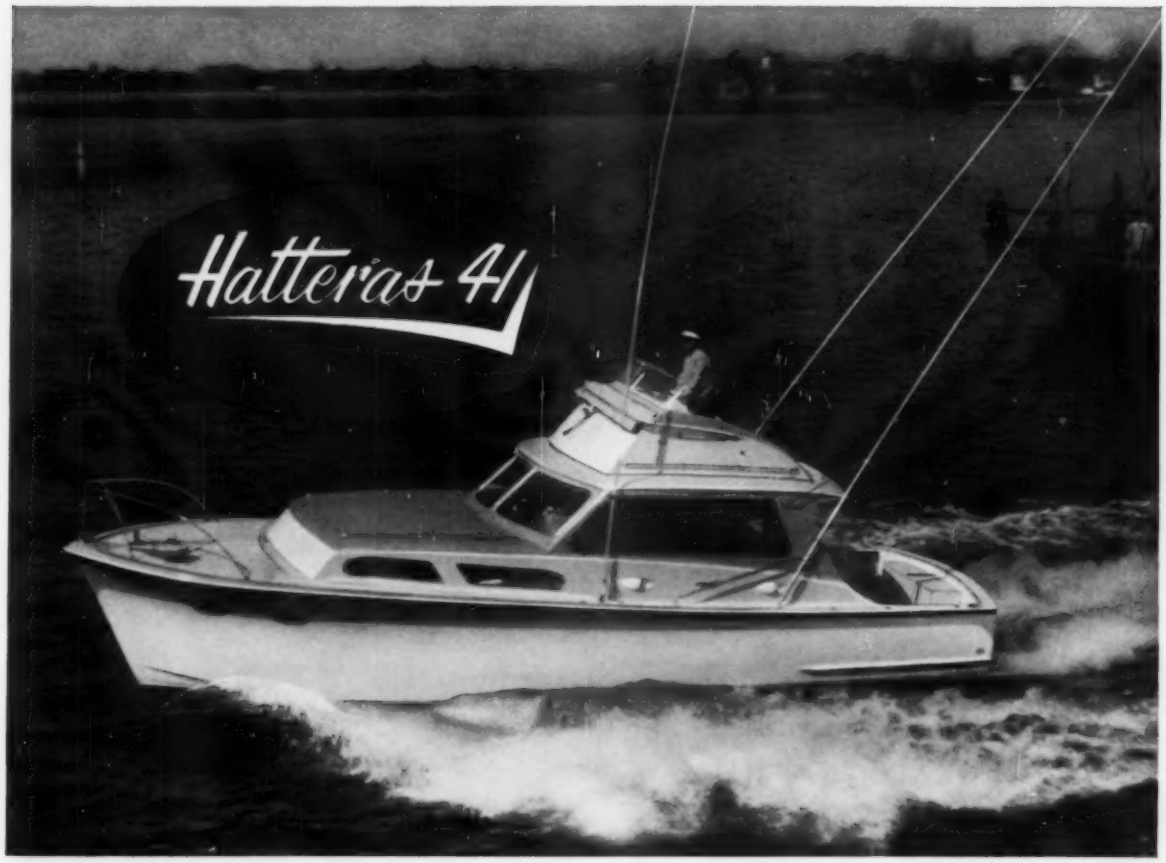
The above describes a specific instance of this application. There are, of course, many other variations that can be employed, each depending on the specific part to be molded. The main economy of two level molding comes about in that smaller presses can be utilized. By having more cavities, shorter runs will yield the production required, thus saving further on labor cost. It, of course must be understood that this process has its limitations in being restricted to shallow lightweight articles.

Multiple Level Injection Molding–the Future

It is conceivable that with careful temperature control, separating the heating of the runner system from the cooling of the molded parts, that hot runner features could be incorporated into the design, a step towards achieving fully-automatic operations.

—■—

Mr. Theodore Saulino, Co-author of this article holds U.S. Patent #2,571,-766 embodying many of the features of design described in this article.



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DOW'S CLINICAL APPROACH TO HEALTHY PLASTICS APPLICATION

TEMPERATURE AND PHYSICAL STRUCTURE DICTATE PLASTICS' WATER VAPOR TRANSMISSION

As with gas permeability, water vapor transmission rate (WVTR) through a plastic barrier is determined by several factors. The most important of these are temperature and composition of the barrier. When the plastic is partially crystalline, the degree of crystallinity also has an important influence on this property.

Water vapor permeability is a function of the diffusion rate and solubility of water vapor in the barrier material. Water vapor apparently permeates by dissolving into the plastic at the incoming surface, establishing a concentration gradient for further penetration. Under the influence of this gradient, the dissolved water vapor diffuses through the plastic superficially in accordance with Fick's Law of diffusion. At the outgoing surface, the penetrant evaporates. Diffusion within the plastic is considered to be the rate-determining factor.

In the case of water molecules diffusing through a hydrophobic polymer, only small concentrations of water will prevail within the polymer. It is expected that Henry's Law will be obeyed and, since the polymer is swollen negligibly by the absorbed water, the diffusion coefficient in Fick's Law should be independent of concentration. In such an ideal system, the permeability coefficient characterizes the transport of water vapor through the polymer. By definition, the permeability coefficient is equal to the product of the solubility coefficient and the diffusion coefficient.

$P = DS$, where:

P = Permeability Coefficient
D = Diffusion Coefficient
S = Solubility Coefficient

An increase in temperature increases the water vapor permeability. Also, the transmission rate varies exponentially with the reciprocal of the absolute temperature ($\log \bar{p}$ vs. $\frac{1}{T_K}$). The linear relationship holds between 35° and 97° C.

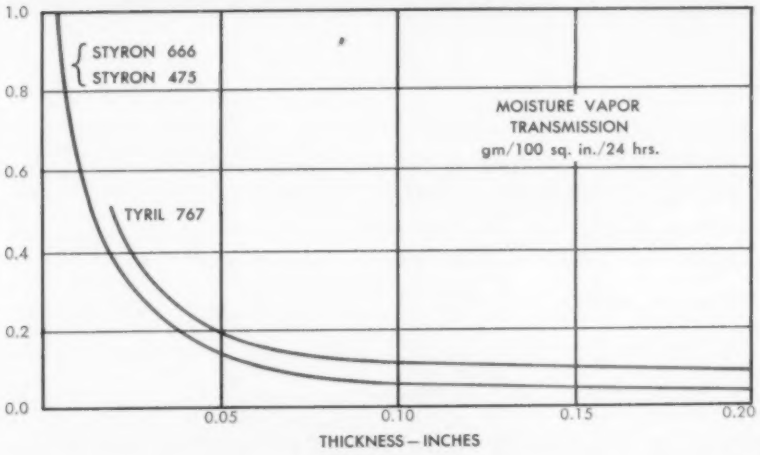
Permeability is directly affected by the molecular structure of the plastic barrier. For example, with partially crystalline polymers such as polyethylene, water vapor transmission is believed to occur almost entirely through the amorphous phase, with little or no transmission through the crystalline phase. Therefore, the amount of penetrant absorbed appears to be in direct proportion to the amorphous material present in the polymer.

One explanation of the negligible degree of vapor permeation through the crystalline phase of the polymer is that there is no free volume to accommodate the water molecule.

In the case of most plastic materials, the water vapor transmission rate is treated as an activated rate process, with the assumption that the water molecules diffuse as holes are formed in the polymer due to segmental motion of the polymer chains. However, in the case of polystyrene it is generally assumed that moisture transport proceeds along submicroscopic cracks or channels, not by the usual mechanism which apparently holds for most other materials. As with all plastic materials having low water absorption, the WVTR for polystyrene is not sensitive to the humidity at which the tests are made.

This study on water vapor permeability is one of a continuing series of Plastiatrics Studies being made by Dow Plastic Technical Service Engineers. For detailed information on this study, and on others covering every area of interest to plastics designers and engineers, write THE DOW CHEMICAL COMPANY, Midland, Michigan, Plastics Sales Department 1803EX9.

CURVES OF WVTR VS. BARRIER THICKNESS FOR THREE DOW PLASTICS.
ASTM METHOD E 96-53T PROCEDURE E
TEMPERATURE 100°F RELATIVE HUMIDITY: 0% IN DISH, 95% OUTSIDE DISH



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SPEAKING OF EXTRUSION

Flow Patterns in a Single-Screw Extruder

This article outlines a simplified theoretical analysis of the flow pattern in the channel of an extruder screw. Photographs of the flow in a transparent model of an extruder are given to support the conclusions of the theoretical discussion.

Screw extruders are widely used to pump highly viscous thermoplastic resins. Among the products produced with the aid of screw extruders are sheet and film, lamination coatings, wire coatings, and rod and tube stock. A better understanding of the process of extrusion is attained by investigation of the flow pattern of the viscous fluid in the channels of the screw. Such an understanding is essential to the sound application of extrusion theory.

A number of papers have been presented on the subject of flow patterns in an extruder channel. Street (*5*) gave a qualitative description of the motion. The diagram of motion given by Carley and Strub (*1*) is incorrect, although their description of the flow as a "helix within a helix" is quite accurate. Eccher and Valentinotti (*2*) took precise measurements of the velocity distribution of fluid in the channel. The photographs taken by Maddock (*3*) show the importance of the rotation of the fluid in the plane transverse to the channel.

The early theoretical analysis of flow in the screw channel considered only the flow in the direction of the screw channel. The flow down the channel was considered to be the difference between the "drag flow" (Q_D) and the "pressure flow" (Q_P). The drag flow was induced by the velocity component of the barrel in the direction of the channel. The pressure flow was caused by the pressure gradient in the direction of the channel and was sometimes spoken of as "backflow". Examples of the velocity profile with channel depth in the direction of the channel are presented in *Figure 1* for several different ratios of pressure flow to drag flow ($a = Q_P/Q_D$). At ratios of pressure:drag flow near 1.0, there is one point at which the downchannel velocity is zero, and the presence of a stagnant layer was thus deduced. Additionally, at high rates of pressure flow, the downchannel velocity is negative near the bottom of the channel, and from this situation the supposition was made that material actually flowed toward the rear of the screw.

Theoretical

The expressions for the velocity profiles in the direction of the channel and in the plane transverse to the channel have been derived previously (*1, 4*). The assumptions made are that: 1. The viscosity is constant at all points in the channel; 2. The bounding surfaces are flat; 3. The channel is very wide compared with the depth; 4. The top surface (barrel) is assumed to move relative to a stationary lower surface (screw). The geometry involved in this discussion is shown in *Figure 2*. To further simplify the discussion, the clearance between screw flight and barrel is taken as zero, i.e., there is no leakage flow over the flight.

The velocity profile in the direction of the channel is given by the expression

$$v = U \cos\phi \ (H - 3a(H - H^2))$$

where

v = Velocity in downchannel direction
U = Velocity of barrel surface
ϕ = Helix angle of screw

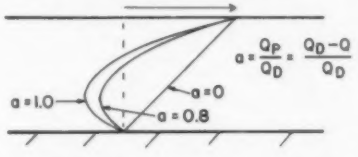

Figure 1. Velocity profile in downchannel direction

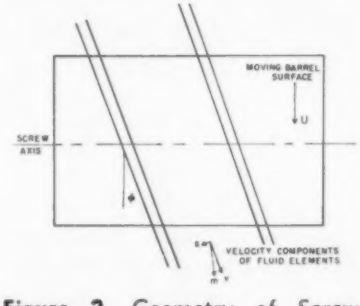

Figure 2. Geometry of Screw Channel

a = Ratio of pressure : drag flows ($a = 0$ for drag flow, $a = 1.0$ for no output)

H = Fractional distance from screw surface to position in channel, the reduced channel depth.

The velocity profile in the plane transverse to the channel is

$$s = U \sin\phi\ (3H^2 - 2H)$$

where

s = Velocity perpendicular to screw flight.

The speed of the fluid at any depth in the channel is given by the vector sum of the two orthogonal components given above.

$$m = \sqrt{v^2 + s^2}$$

$$= \sqrt{(U \cos\phi\ (H - 3a(H - H^2)))^2}$$

Quantity below included under square root sign

$$+ (U \sin\phi\ (3H^2 - 2H))^2$$

A plot of the speed (m/U) as a function of the reduced channel depth, H, for a helix angle of 17.7° and for a range of values of a is given in *Figure 3*. At the barrel surface (H = 1.0), the speed of the fluid is that of the barrel (m/U = 1.0) for all degrees of pressure flow. At the root of the screw (H = 0), the speed of the fluid is zero for all degrees of pressure flow. At intermediate depths in the channel, the speed of the fluid depends on the degree of pressure flow, but it should be noted that the fluid speed is zero at any point only for the value of a (1.0) which corresponds to no output from the screw.

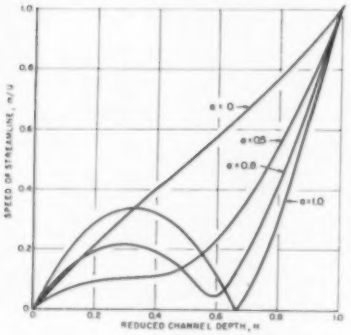

Figure 3. Speed of fluid as a function of channel depth for different degrees of pressure flow.

The direction in which a particle of fluid in the channel moves is the second important bit of information necessary to describe the flow pattern in the channel. The direction will be specified here by the angle that a streamline makes with a plane perpendicular to the axis of the screw. An angle of zero will correspond to the direction of movement of the barrel surface, and positive angles to 180° will be in the direction of the net flow of the fluid under conditions of no pressure gradient, i.e., toward the output end.

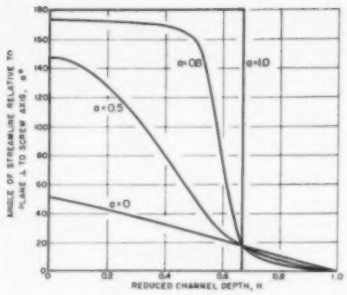

Figure 4. Angle of streamline as a function of channel depth for different degrees of pressure flow

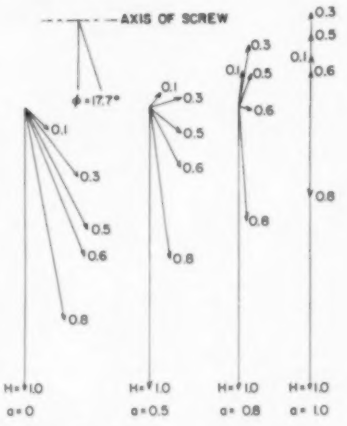

Figure 5. Velocity at different depths in the channel for four degrees of pressure flow

Giving the symbol α to the angle of the streamline relative to a plane perpendicular to the axis of the screw, the angle is related to the two velocity components by the expression

$$\tan\alpha = \frac{v \sin\phi - s \cos\phi}{v \cos\phi - s \sin\phi}$$

$$= \frac{\cos\phi(H - 3a(H - H^2))\sin\phi}{\cos^2\phi(H - 3a(H - H^2))}$$

Quantity below part of fraction above

$$\frac{-\sin\phi(3H^2 - 2H)\cos\phi}{+\sin^2\phi(3H^2 - 2H)}$$

The angle of flow relative to a plane perpendicular to the axis of the screw (α) is plotted in *Figure 4* as a function of reduced channel depth (H) for different ratios of pressure : drag flow (a); the helix angle has again been taken as 17.7°. At the barrel surface (H = 1.0) the angle of flow is zero for all ratios of pressure : drag flow, corresponding to movement in the direction of the barrel surface. At H = 0.67 (2/3), the angle of flow is 17.7°, the helix angle used in this illustration; at H = 0.67, the velocity perpendicular to the screw flight (s) is zero, and flow must be in the direction of the channel for all degrees of pressure flow. At the screw surface (H = 0) the angle varies from 50° at no pressure flow to 180° at a pressure flow sufficient for no output from the extruder (a = 1.0). With no output from the extruder, the angle of movement is either 0 or 180°, that is, in the plane perpendicular to the screw axis.

The important conclusion from *Figure 3* is that the angle of movement of fluid is always between 0 and 180° for the entire range of channel depths and for all usual ranges of pressure flow (a = 0 to 1.0). This means that all of the fluid is always moving toward the output end of the extruder, as long as there exists any output whatsoever. In the direction of the channel, material appears to be moving backward for some conditions of pressure flow, but in the direction of the axis of the screw no backward movement ever exists. The term "backflow" is thus something of a misnomer, and an understanding of the full meaning of the term is important.

The data presented in *Figures 3 and 4* may be plotted in polar form to give a slightly different method of expression. The data for a = 0, 0.5, 0.8, and 1.0 are plotted in this fashion in *Figure 5*. The conclusion is again reached that fluid moves only forward relative to the direction of the axis of the screw.

Experimental

A model of an extruder was constructed with a transparent barrel which could be caused to rotate about a stationary screw. The diameter of the screw was 3.5 in., the lead of the screw was 3.5 in. (outer helix angle was 17.7°), the channel depth was 0.625 in., and the width of flight in the direction of the screw axis was 0.40 in. The total length of the screw section was 23.4 in., and the length of the barrel was 17.0 in. The screw was centered axially in the barrel and thus protruded past the end of the barrel into chambers which had a large crosssectional area relative to

that of the screw so as to minimize entrance and exit effects. The fluid entered the inlet chamber from a large reservoir through a 1¼ close nipple. The fluid left the discharge chamber through 6 inches of 1¼ in. pipe. The fluid used in the study was 43° Be. corn syrup, possessing a viscosity in the order of 1000 poise at room temperature.

The flow through the equipment was altered by changing the size of a restriction in the outlet pipe. With no additional restriction, the flow was about 95% of the calculated drag flow. Various restrictions were employed to give flow from this value down to zero. The barrel was rotated at a speed of 1 RPM by means of a chain drive from a gear reducer on a variable-speed hydraulic unit.

A small-diameter probe was installed at the center of the screw in the middle of the channel. The probe, made of hypodermic tubing, had the outlet end plugged. A number of short, small tubes were installed at right angles to the probe, the small tubes being spaced along the length of the probe. The probe was perpendicular to the screw surface and extended to within 1/32 in. of the barrel surface. The inlet end of the probe passed into the hollow core of the screw and was connected to a syringe. In this way a number of discrete streams of fluid colored with an intense black could be injected continuously.

At constant rotational speed of the barrel, the volumetric flow rate of fluid was determined by means of a graduated cylinder and stopwatch. The rotational speed of the barrel was measured by timing the rotation through a given number of revolutions. The black fluid was slowly injected through the probe, and a photograph taken with the axis of the probe pointing directly toward the camera.

Photographs taken of the fluid being injected through the probe are shown in *Figures 6-9* in which the ratios of pressure:drag flow are 0.07, 0.41, 0.61, and 1.0, respectively. The traces of black fluid in the clear bulk fluid appear as a fan-shaped pattern, the higher the ratio of pressure:drag flow the wider the spread of the fan. The black line to the rear of the probe was a circumferential line drawn on the rotating barrel to give an accurate record of the line of barrel motion.

Discussion

The photographs of the flow patterns in an extruder channel presented in *Figures 6-9* demonstrate conclusively that no fluid in the channel ever moves toward the rear of the extruder, so long as there is a net output from the extruder.

With the photographs of *Figures 6-9* so oriented as to view the flow in the direction of the channel, flow at the bottom of the channel does appear to be going back up the channel. The point to be made is that the velocity profile in the plane transverse to the channel must be included to obtain an adequate picture of flow in the channel, and this crosschannel flow may have an important component in the direction of the axis of the screw. During the time the material at the bottom of the channel appears to be going rearward in the channel, it is also moving toward the front edge of the channel, and the net motion is towards the output end of the extruder.

The theoretical equations were presented for a simplified system in which plane, parallel surfaces caused the motion of fluid. Investigation of the flow speed and direction in the circular case in which the thread depth is a significant fraction of the screw radius shows that the same conclusions are reached as for the simplified case. The photographs of flow patterns shown in *Figures 6-9* were made of flow in a screw channel in which the thread depth was 36% of the screw radius. The assumptions of the simplified analysis would not be expected to apply exactly to this case, yet the similarity of *Figure 5* to *Figures 6-9* is unmistakable. The qualitative conclusions reached from an examination of either set would be identical.

The assumption of constant viscosity throughout the fluid was made in the simplified analysis. An isothermal Newtonian fluid was used for the simulation. The question arises as to whether, in an extruder where temperature is not constant over the channel and which is pumping a non-

Photographs of flow streamlines in an extruder channel

Figure 6. Ratio of Pressure: Drag Flow (a) = 0.07

Figure 7. Ratio of Pressure: Drag Flow (a) = 0.41

Figure 8. Ratio of Pressure: Drag Flow (a) = 0.61

Figure 9. Ratio of Pressure: Drag Flow (a) = 1.0

Newtonian elastic melt, the conclusion that no material moves toward the rear of the extruder would still be valid. No experimental evidence on this score has been obtained, and so the limitation of the above conclusions must be recognized as applying to a system of constant fluid viscosity.

Nomenclature

- a Ratio of pressure:drag flow in extruder channel
- H Fractional distance from screw surface to position in channel, the reduced channel depth
- m Speed of streamline in channel
- Q_D Volumetric output of extruder with zero pressure gradient
- Q_P Volumetric flow through extruder under influence of pressure gradient, screw stationary
- s Speed of fluid in plane transverse to channel
- U Velocity of moving barrel surface
- v Speed of fluid in channel direction
- α Angle of fluid streamline relative to plane perpendicular to axis of screw
- ϕ Screw helix angle

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edited by

Bruce H. Maddock,

Union Carbide Plastics Co.

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FIGHTING CORROSION WITH PLASTICS . . .

Subject of San Francisco Regional Technical Conference

"Plastics vs. Corrosion" will be the theme of an SPE Regional Technical Conference (RETEC) to be held in San Francisco on October 5 at the Mark Hopkins Hotel. Sponsored by the Golden Gate Section of the Society of Plastics Engineers, the one-day technical meeting is under the General Chairmanship of Dr. J. W. Richardson of Rohm & Haas Co., San Francisco.

Objective of the Conference is to broaden the knowledge of those engaged in combatting corrosion by introducing and increasing the use of plastics in this important area. Many structures, valves, piping systems, tanks and coatings are constantly being destroyed by corrosive action of salt water, acids and other agents, amounting to multi-million-dollar losses annually. Speakers at the Conference will indicate low-cost and efficient methods to cut down maintenance and replacement costs by use of the plastics materials.

The Conference will be supplemented on October 6 and 7 by a regional meeting of the National Association of Corrosion Engineers in the same city at the Sheraton-Palace Hotel. The three consecutive days of discussion of corrosion problems are expected to attract representatives of a wide variety of Bay Area industries, including petroleum refining, food processing, chemical processing, maintenance and others.

The technical program for the SPE RETEC announced by Program Chairman John Joyce of Western Plastics Magazine, San Francisco, includes the following papers:

- **Trends in Plastics as Materials of Construction for Corrosion Resistant Applications**
  Dr. Raymond B. Seymour, Sul Ross State College, Alpine, Texas
- **Polyesters as Corrosion-Resistant Coatings**
  Neil S. Estrada, Reichhold Chemicals
- **Uses of 'Penton' Chlorinated Polyether as a Chemical-Resistant Plastic**
  George M. Taylor, Hercules Co.
- **Chemical Resistance Properties of Molded Diallyl Phthalate Plastics**
  David E. Cordier, Mesa Plastics Co.
- **A New System of Large Structures of Glass Fibers and Polyesters**
  John Heidacher, CTL Division, Studebaker Packard Corporation
- **Use of Thermoplastic Piping Systems for Corrosion Service**
  Jack G. Fuller, Jr., Chemtrol
- **High Density Polyolefins—Their Applications in Corrosion Engineering**
  O. E. Larsen, Phillips Chemical Co.
- **Vinyl Plastisols in Corrosion Applications**
  (Speaker to be Announced), B. F. Goodrich Chemical Co.
- **New Pumps from Old, via Plastics**
  S. E. Susman, Narmco Industries, Inc.
- **Corrosion (a film on corrosion protection of steel pipe with plastics materials)**
  (Speaker to be Announced), Koppers Co., Inc.
- **Combatting Corrosion with Butyrate Pipe**
  W. P. Gideon, Eastman Chemical Products, Inc.

Speaker at the Conference Luncheon will be George W. Martin, SPE President, who will discuss Society activities in an address "The Progress and Future of SPE". Also, Society Executive Secretary Thomas A. Bissell will detail operation and functions of the Executive Office.

Organization of the RETEC is under the direction of the following committee chairmen:

Publicity, Frederic M. Rea, Western Plastics Magazine, San Francisco; Printing, Robert S. Elliott, Royell, Inc., Palo Alto, Calif.; Hospitality, Robert L. Skov, Hercules Powder Co., San Francisco; House, L. G. Maclise, Dow Chemical Co., San Francisco; Treasurer, Robert J. Wnukowski, Tools, Dies and Molds, San Francisco; and Moderator, Frank D. Allen, L. H. Butcher Co., San Francisco.

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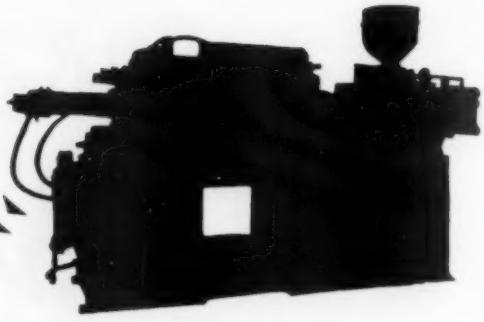

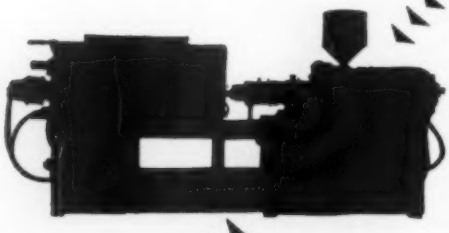

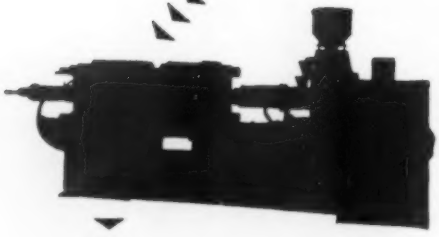

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MOLDING CYCLES

Some Mold Fill Time Considerations

Today's trends in the injection molding field are in the direction of faster filling time along with faster cycling time due to overall speeding up of the opening and closing of the machines. Faster filling time has resulted in some advantages which have not been noticed and in some which have been deliberately sought.

There are advantages and difficulties which need to be weighed carefully with a full knowledge of a few fundamental facts in mind. It is possible to obtain excellent results from fast filling time if the whole story is well understood.

Power requirements for fast filling are higher than for conventional molding in most cases. Tooling costs are also higher because molds have to be built to take advantage of the full range of high speed filling benefits. High speed filling appears not to work well in some molds for reasons which have been difficult to explain, but at the same time it has been amazingly successful in other molds. The physical properties of parts molded by high speed filling are usually improved considerably, and generally they are more consistent from one part to another.

Some of the critical points with regard to mold filling time may be explained in the following discussion.

Chilling Against the Mold Wall

The wall of an injection mold is usually much cooler than the temperature of the melted plastic which is being forced into the mold. The plastic which comes in contact with the wall is chilled immediately to a temperature below that which easy flow occurs. Noncrystalline plastics such as polystyrene and cellulosics orient along the mold wall, and the layer of oriented material is different from the unoriented material beneath this skin of plastic. The depth of skin for polystyrene was found to be approximately .020 inch when the wall thickness was .170 inch in an experimental mold. This mold was filled relatively slowly because there was not any widespread application of high speed filling in the days when this experiment was run.

The depth of the chilled skin indicates the mold ought to be filled quickly if it is to be filled at all especially if the wall thickness is in the order of .035 inch or less. It would seem to be impossible to fill a mold with .035 inch plastic thickness if the chill is .020 inch thick from each side. It is probably true the mold could not be filled in the days when the experiment described above was run. It is known that very few people tried to mold plastic this thin at that time.

The usual practice in injection molding is to keep the mold surface warm, and some molders keep the mold fairly hot. They like to have the mold approximately 10°F. lower in temperature than the heat distortion temperature of the plastic material. This prevents excessive chilling and is an aid to filling the mold. It is very reasonable to believe the depth of chill is somehow connected with the time of contact between the plastic and the mold wall. Sooner or later, the plastic will become chilled to the mold temperature if it is left in the mold long enough. Furthermore, it seems reasonable to expect the infinitesimally thin skin of plastic immediately next to the mold wall is chilled to the mold wall temperature instantaneously upon contact.

The difference between the instantaneous time of chilling and the long time to reach equilibrium between plastic and mold wall is not very great. The mold fill time is significant in the build-up of skin thickness.

This reasoning indicates fast filling time can allow the mold wall to be cooler without interfering with the flow of the plastic. Some people believe it is advisable to keep the mold wall cool for best results in removing the heat from the plastic quickly and thereby shortening the overall molding cycle. This leads one to suppose fast fill time can result in faster molding cycles through the use of colder mold walls. This is a bonus in addition to the time saved on the injection cycle through faster filling.

Crystallization and Orientation

Crystalline plastics should be completely melted before they are forced into a mold. This is very seldom accomplished because of the practical difficulties of handling an extremely fluid material. Consequently, it is difficult to know what percentage of crystals are melted and what percent remains unmelted or in a gel form. Furthermore, some crystalline plastics begin to crystallize within less than one second after they have been quenched to the crystallizing temperature. Rapid mold filling is actually a necessity for producing good and consistent parts of such materials. These parts may be difficult to control in dimensions because crystallization varies in rate and amount. The chilling action of the mold wall can vary the physical properties of the part, and it seems reasonable to believe faster fill time would reduce the influence of the mold wall chilling.

Noncrystalline plastics orient, and orientation can be a cause of inconsistent properties. Orientation occurs in a temperature range above 200°F.

and below the molding temperature. The orientation range varies according to the material. Fast filling tends to reduce the thickness of the oriented layer, and therefore it should reduce the influence of this layer upon the physical properties and dimensional stability of the molded part.

Quantity Control Needs

High speed mold filling requires sharp control of the quantity of material which is forced into the mold. The plastic is still very fluid when it is forced into the mold rapidly, and it is necessary to stop pressing it once the mold is full. Deep draw parts stick in the mold very readily if too much material is placed there. Large area parts tend to cause the mold to separate and, while flash does not ordinarily form until the mold has opened approximately .020 inch, thicker parts require more material and therefore are not profitable.

The residual fluidity of the plastic after the mold is full has a considerable effect upon the ability to avoid sink marks. Sink marks will not occur if the mold is sufficiently full of plastic before the plastic starts to cool. If the mold fill time is short enough, the plastic will be fluid enough to flow into all parts of the mold and distribute itself under reasonably uniform pressure conditions. Slow filling results in difficulty of transmission of pressure throughout the mold and often results in inability to place sufficient plastic in the heavy sections, because the thinner sections through which that plastic must flow have become so stiff the material cannot be transferred to the heavier section.

Fill time is becoming shorter and shorter, and the stage is approaching in which it will be necessary to provide air venting, which consists of considerably more than a few scratches at the mold parting face where the plastic appears to be burning. Mold fill time from .5 second downward should demand special venting considerations to obtain the best results from the faster mold filling facilities. Under such conditions the air in the mold is compressed very rapidly, and it provides an appreciable resistance to filling by itself. This resistance requires much more power to force the plastic into the mold than would be required if the air were removed. When the mold fill time is of the order of .1 second or less, it may be necessary to evacuate the air from the mold to some extent. In the die casting field, mold fill times are sometimes recorded to be considerably less than .1 second, and in such cases venting the air is a problem which the mold designer has to consider. There is not much reason why this problem should not be considered by the designer of plastic molds, too.

Trends in Machinery Today

Injection molding machines have been built with larger power plants and more efficient plasticizing units. Impact molding, sequential impact molding, valve gate molding, and preplasticizing machines are all factors which have brought about doubling or tripling the average mold filling speed. In some cases, molds have been reported to be filled as much as six times as fast by these new methods than was possible to fill them previously.

Stories of these results have been passed around in some of the literature and by word of mouth. The progress of the new methods seems to be slow, and certainly has been expensive. It is difficult to reach ideal conditions, but it seems to be correct to aim for them rather than to aim in some other direction or not to aim at all.

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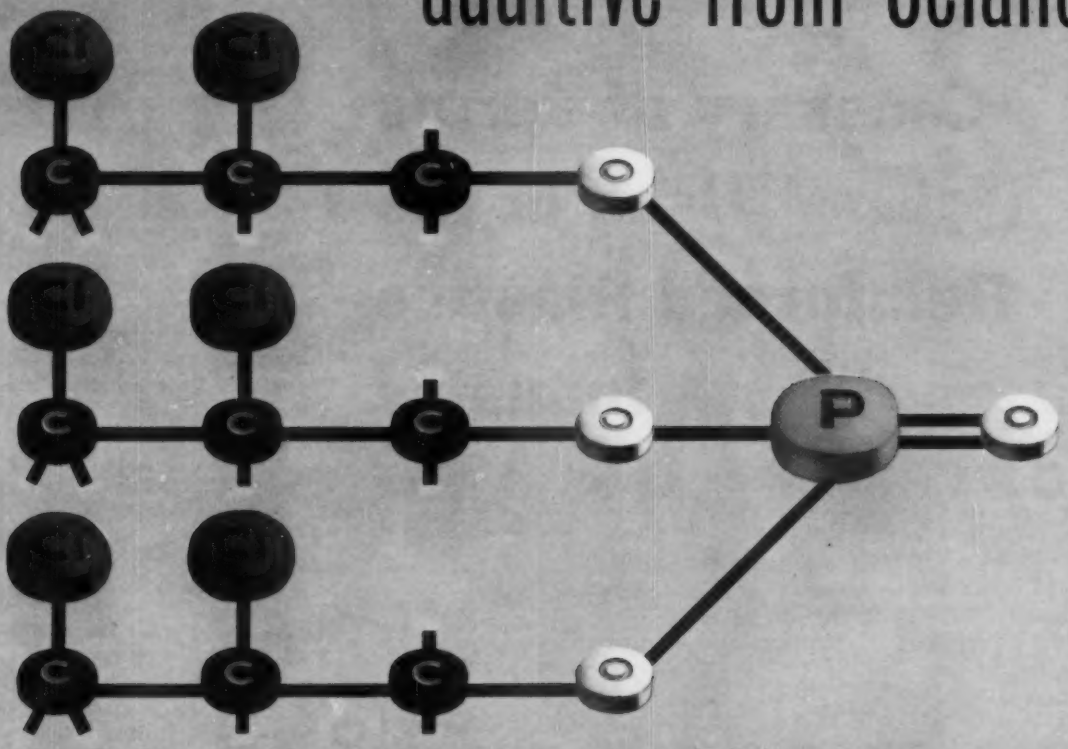

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REINFORCED PLASTICS

Glossary of Terms Used in the Reinforced Plastics Industry

Accelerator:
An agent used to hasten a reaction so as to reduce the time required for a thermosetting resin to cure or harden.

After-Bake:
See *Post-Cure*.

Back Pressure:
Resistance of a material, due to its viscosity, to continued flow when mold is closing.

Bag Molding:
Application of fluid pressure, usually air or vacuum, to a flexible membrane or bag enclosing the material to be molded.

Ball Mill:
A cylindrical mill containing steel, porcelain or flint balls within the revolving cylinder which supply the grinding action and reduce the size of the particles present in the material being milled.

Banbury Mixer:
A mixing, converting, or densifying apparatus consisting of two rotors enclosed in a mixing chamber, which may be either heated or cooled.

Binder:
1. The resin or cementing constituent of a plastics compound responsible for the adhesive forces which hold the other components together.
2. Also, the agent applied to mat or preforms to bond the fibers prior to laminating or molding.

Blister:
Round elevation on the surface of a polyester resin, somewhat resembling a blister on human skin.

Blocking:
An undesired adhesion between touching layers of a material, such as occurs during pressure in storage.

Blooming:
Irregular, cloudy or greasy appearance of surface of polyester resin.

Bubble:
A globule of air or other gas trapped within a plastic.

Bulk Factor:
The ratio of the volume of loose molding compound to the volume of the molded part made from it.

Bulking Value:
Volume of a unit weight usually expressed as gallons per pound.

Burned:
Showing evidence of thermal decomposition through some discoloration, distortion, or destruction of the surface of the plastic. See also *Discoloration*.

Calender:
To prepare sheets of material by pressure between two or more revolving rollers. Used in connection with preparation of films and coating of materials.

Casting:
The finished product of a casting operation; should not be used as synonym for molding.

Chalking:
Dry, chalk-like appearance of or deposit on surface of plastic.

Charge:
The measurement or weight of material, either liquid, preformed, or powder used to load a mold.

Cohesion:
The state in which particles of single substance are held together by primary or secondary valence bonds.

Cold Flow:
The distortion which takes place in materials under load at room temperature. See *Creep*.

Cold Molding:
A procedure in which a composition is shaped at room temperature and hardened by subsequent baking.

Cold Pressing:
A bonding operation in which the adhesive sets under pressure without application of heat, *i.e.*, at room temperature.

Condensation:
A chemical reaction in which two or more molecules combine with the separation of water. If a polymer is formed, the process is called polycondensation. See also *Polymerization*.

Condensation Resins:
Any of the alkyd, phenol-aldehyde or urea formaldehyde resins. The final products are also called condensation polymers. See *Polymerization*.

Cooling Fixture:
A fixture used to maintain the shape or dimensional accuracy of a molding or casting after it is removed from the mold and until the material is cool enough to retain its shape.

Core Pin:
A pin for forming a hole or opening in a molded piece.

Crazing:
Fine cracks which may extend in a network on or under the surface of a casting or a molding.

Creep:
Following the initial instantaneous elastic deformation, the dimensional change with time of a material under load. Creep at room temperature is sometimes called *Cold Flow*.

Cross-Laminate:
A laminate in which some, usually alternate, layers of material are obtained at right angles to the strongest direction of the material in tension.

Cure:
To change the physical properties of a material by chemical reaction, which may be condensation, polymerization or vulcanization; usually accomplished by the action of heat and catalysts, alone or in combination with pressure.

Cycle:
One complete operation of a molding press from closing time to closing time.

Daylight Opening:
Space between two platens when a press is open.

Discoloration:
Deviation from accepted standards of color.

Dished:
A symmetrical distortion in a molding, casting, or laminate which makes a section of it appear concave, a curved section more concave. See *Warp*.

Domed:
A symmetrical distortion which makes a flat section of an object appear convex, a curved section more convex. See *Warp*.

Draft:
The taper or slope of the vertical surfaces of a mold designed to facilitate removal of molded parts.

Draw:
To stretch a sheet of plastics material to fit a mold. To cup.

Dry Spot:
Area in which reinforcement has not been wetted by resin.

Edge Bowing:
Inward bowing, characteristic of edges of open boxes.

Ejector:
A pin or other device for removing finished piece from mold.

Elastomer:
Any compound having elastic properties.

Endothermic Reaction:
A reaction which absorbs heat.

Exothermic Reaction:
A reaction which liberates heat.

Fiber Orientation:
Fiber alignment in direction of flow giving strength in one direction only.

Fiber Pattern:
Visible fibers on surface of laminate or molding.

Filler Specks:
Specks of filler which stand out in contrasting color against a plastic binder.

Fines:
Pulverized particles of grains or fibers accompanying larger ones.

Fish Eye:
In a transparent or translucent plastic, any small, globular mass, which has not blended completely into the surrounding material.

Flash:
The excess molding material which runs out of the cut-off when a mold is closed.

Flash Mold:
A mold designed to permit escape of excess molding material. Such a mold relies upon back pressure to seal the mold and put the piece under pressure.

Flow:
1. The movement of resin under pressure, allowing it to fill all parts of a mold.
2. Flow or "creep": The gradual but continuous distortion of a material under continued load, usually at high temperatures.

Gel:
1. The name given to any gelatinous mass.
2. The "stage" at which a polymerizing resin composition thickens to a semi-solid state.

Gelation:
The formation of a gel.

Guide Pins:
Devices that maintain proper alignment of mold sections during closure.

Haze, Internal:
An indefinite cloudy mass within a transparent plastic.

Haze, Surface:
An indefinite cloudy area on the surface of a plastic; not described by *Chalking* or *Lubricant Bloom*.

Heat-Convertible Resin:
A thermosetting resin convertible by heat to an infusible and insoluble mass.

High Pressure Spot:
An area containing very little resin. Usually due to excess of reinforcing materials.

Hobbing:
Forming a mold cavity by forcing a hardened master model in a soft steel block.

Hydrophilic:
Capable of adsorbing or absorbing water.

Hydrophobic:
Capable of repelling water.

Inert:
Not chemically reactive.

Infusible:
Not melting under heat.

Inhibitor:
A substance which retards a chemical reaction; used in certain types of monomers and resins to prolong storage life.

Isomers:
Two or more compounds having the same kind and number of atoms but with different molecular structures or properties.

Laminate:
To unite sheets of material by a bonding material, usually with pressure and heat. Normally used with reference to flat sheets.

Lake:
See *Shrinkage Pool*.

Land:
The portion of a mold which provides the separation or cutoff of the flash from the molded piece. The horizontal bearing surface of a semi-positive or flash mold.

Lay-Up:
The arrangement of reinforcing material and the resin in its uncured state.

Light Stable:
Resistant to change upon exposure to light.

Linear Molecule:
A straight-chain molecule.

Low-Pressure Molding:
The distribution of relatively uniform low pressure over a resin-bearing fibrous assembly of cellulose, glass, asbestos or other material, with or without application of heat from external source, to form a structure possessing definite physical properties.

Lubricant Bloom:
An irregular, cloudy, greasy exudation on the surface of a plastic.

Mat, Bonded:
A sheet of fibers held together with a binding agent.

Matte:
A non-specular surface having diffused reflective powers.

Mechanical Adhesion:
Adhesion between surfaces in which the adhesive holds the parts together by interlocking action. See also *Specific Adhesion*.

Mold Marks:
A defect or parting line in a mold which is imparted to the molded material.

Mottle:
The desired or accidental mixture of colors or shades of a color giving more or less distinct or complicated pattern or specks, spots, or streaks of color.

Opalescence:
In reference with the clarity of vision through a sheet of transparent plastic at any angle because of diffusion within or on the surface of the plastic.

Open Bubble:
A bubble which has partially broken through the surface of a plastic. See also *Bubble*.

Orange Peel:
An uneven surface somewhat resembling that of an orange peel.

Parallel Laminated:
A laminate in which all the layers of materials are oriented parallel to the strongest direction in tension.

Parting Line:
A mark on a molded piece where sections of a mold have met in closing.

Pinhole:
A tiny hole in surface of, or through, a plastic material—usually occurs in multiples.

Pit:
A small regular or irregular hole in the surface of a plastic, usually has approximately the same diameter as depth, and is often dull or rough at the bottom.

Positive Mold:
A mold designed to apply pressure to a piece being molded with no escape of material.

Post-Cure:
In certain resins, complete cure and ultimate mechanical properties are attained only by exposure of the cured resin to higher temperatures than those of curing. This second stage, the post-cure, is necessitated by the fact that the higher temperatures would result in excessive reaction if used throughout the entire cure.

Pot Life:
The time between complete catalyzation and initial gelation, during which time a resin mix is said to be usable. Also called *Working Life*.

Power Factors:
In an insulating material, the power factor is the ratio of total power loss (watts) in the material to the product of voltage and current in a capacitor in which the material is a dielectric. Also, the cosine of the angle between the vectors of applied voltage and current flowing in the circuit.

Preform:
1. A preshaped fibrous reinforcement formed by distribution of chopped fibers by air, water flotation, or vacuum over the surface of a perforated screen to the approximate contour and thickness desired in the finished part.
2. A preshaped fibrous reinforcement of mat or cloth formed to desired shape on a mandrel or mock-up prior to being placed in mold press.
3. A compact pill formed by compressing pre-mixed material to facilitate handling and control of uniformity of charges for mold leading.

Premix:
A molding compound prepared prior to and apart from molding operations and containing all components required for molding. These are resin, fibrous reinforcement in chopped form, fillers, catalysts, release agents, and other compounds.

Prepreg:
Ready-to-mold material in web form which may be cloth, mat or paper impregnated with resin and stored for use.

Press Polish:
A high-sheen finish on sheet stock produced by contact, under heat and pressure, with a very smooth surface.

Reinforcement:
Material used primarily for strengthening a plastic product. Such materials may be fibrous glass, or cotton which are impregnated with the plastic mixture. *Reinforcement* should not be used synonymously with *Filler*.

Resin-Rich Area:
Space which is filled with resin and little or no reinforcing material.

Ripple:
Wavy or irregular surface, usually a result of fiber washing or wrinkling of reinforcement.

Room-Temperature-Setting Adhesive:
An adhesive which sets at 68 to 86°F. inclusive. These are the limits for room temperature specified by ASTM Standards (D618-51T).

Satin:
A plastic finish having a satin or velvety appearance.

Scratch:
Shallow mark, groove, furrow, or channel.

Semi-Positive Mold:
A mold which permits the escape of a small amount of material when it is closed.

Set:
To convert a resin into a fixed or hardened state by chemical or physical action, such as condensation, polymerization, vulcanization or gelation. See also *Cure*.

Short:
An incompletely filled out condition in a molding caused by insufficient quantity of resin or by the resin setting up before proper pressure is applied. The latter is also referred to as *Precure*.

Shrinkage Pool:
An irregular, slightly depressed area on the surface of molding caused by uneven shrinkage before complete hardening is attained. Also called *Lake*.

Size:
A coating composition for sealing porous surfaces prior to further finishing.

Warp:
Dimensional distortion in a part after molding or other fabrication.

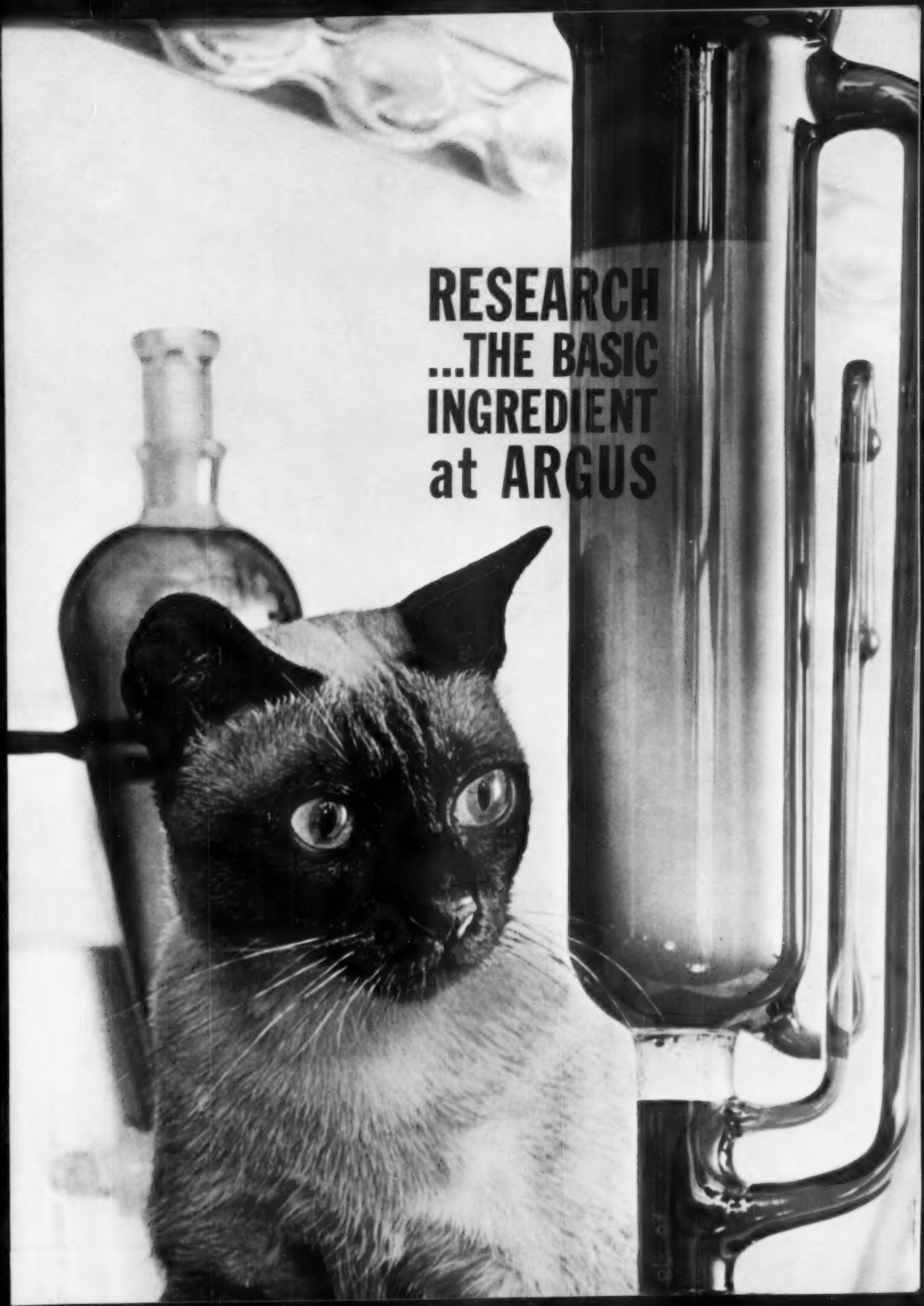
Washing:
Abnormal tearing or displacement of the reinforcing material during molding.

—— ■ ——

edited by

George Lubin,

Grumman Aircraft Co.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Primary Selector Guide

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Calendered Vinyl	Film
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	Sheeting
	Crystal Clear Rigid PVC
	Translucent Rigid PVC
	Semi-Rigid PVC
	Non-Toxic
Extruded Vinyl	Crystal Clears
	Opaque
	Electrical Insulation
	Non-Toxic
Plastisols, Organisols & Vinyl Solutions	Coating Applications
	Slush and Rotational Molding
	Rigidsols
	Dip Molding
	Solution Coatings
	Non-Toxic
Floor Tile Compounds	Vinyl Asbestos
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long line of Argus "firsts" are the improved, non-toxic stabilizers for rigid vinyls: Mark 33, 34 and 35.

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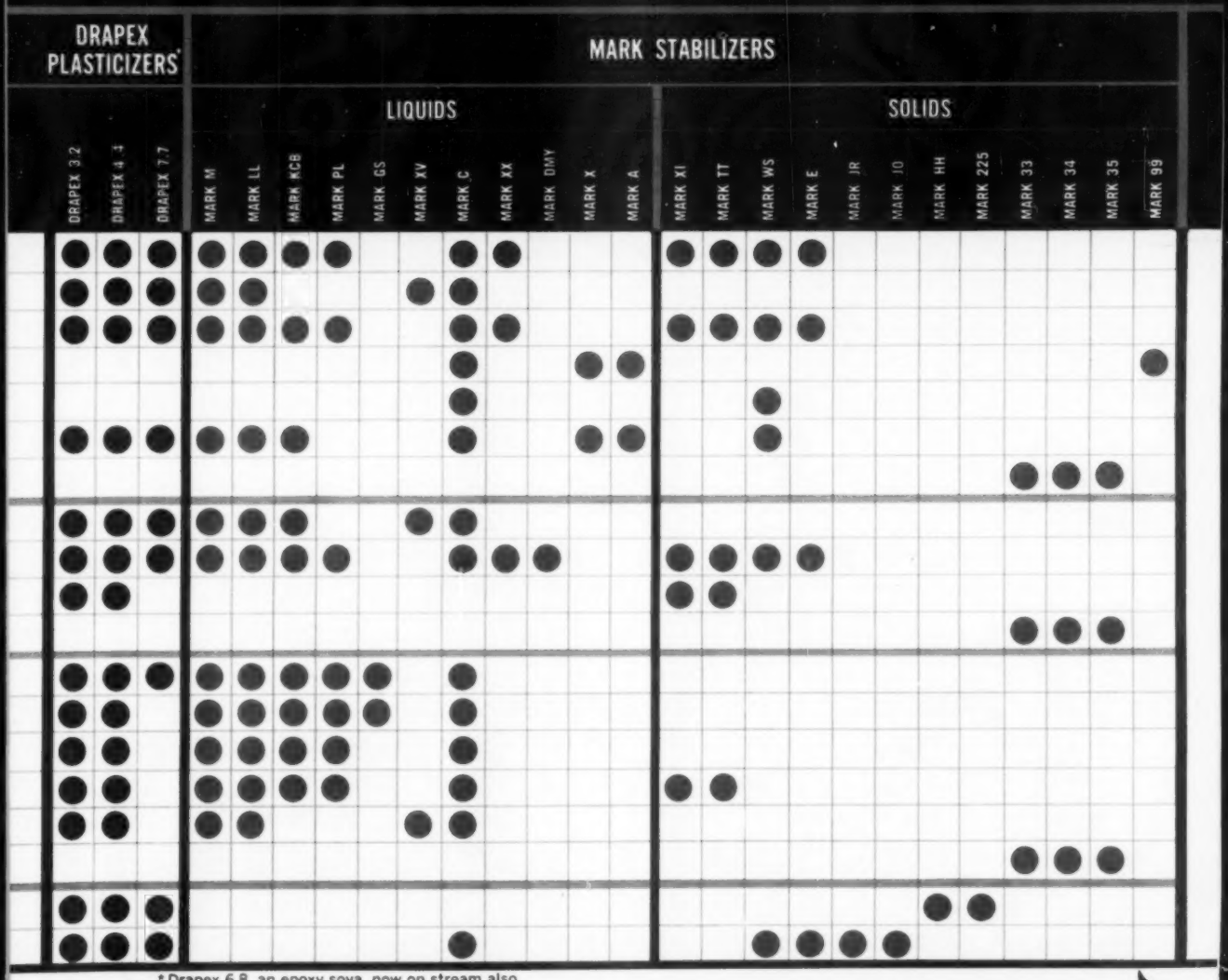

* Drapex 6.8, an epoxy soya, now on stream also.

The characteristics of Argus Mark Stabilizers and Drapex Plasticizers are described on the following page.

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The following information will help you select the right stabilizers and plasticizers for specific needs.

Liquid Stabilizers

MARK M Barium-cadmium complex. Gives outstanding heat and light stability, and excellent initial color. Makes possible high temperature processing without the development of yellow undertones.

MARK LL Newest general purpose barium-cadmium stabilizer. Gives more heat and light stability, and better retention of the true tones of sensitive organic pigments, than any other stabilizer on the market. May be used with all suspension homopolymer resins.

MARK KCB Barium-cadmium-zinc complex. Recommended for resistance to sulfide staining. Also gives outstanding heat stability to all vinyl compounds highly filled with calcium carbonate, regardless of resin choice.

MARK PL Zinc-containing complex. Exhibits a synergistic action on stability and provides high resistance to sulfide staining, when used with other Mark stabilizers.

MARK GS Zinc-containing complex for plastisols. Provides outstanding air release or "bubble break" characteristics, and complete freedom from mold plate-out.

MARK XV Cadmium-containing chelating agent. Markedly improves the heat and light stabilizing action of lead, barium, calcium and strontium stabilizers. Recommended as sole stabilizer for applications requiring light stability and crystal clarity.

MARK C Most efficient chelating agent developed. Used with barium-cadmium systems, it improves heat stability, provides crisper color and superior clarity. Specifically recommended for compounds containing high amounts of phosphate plasticizers.

MARK XX Antioxidant or chelating agent. Increases the efficiency of a saturated metallic soap or a metallic salt.

MARK DMY Chelating agent. Developed specifically for applications requiring extreme long-term stability.

MARK X & MARK A Alkyl tin mercaptides. Specifically recommended for stabilizing crystal-clear unplasticized compounds and certain European emulsion polymerized resins which may be difficult to stabilize with conventional barium-cadmium stabilizers.

MARK XI Coprecipitated barium-cadmium laurate. Provides excellent heat and light stabilization. Also, used with Mark M or LL, it is recommended for stabilizing compounds containing more than five parts of a phosphate plasticizer.

Solid Stabilizers

MARK TT Barium-cadmium soap, generally interchangeable with Mark XI. Recommended for stabilizing high-phosphate formulations as well as all general purpose vinyl applications. Gives excellent heat stability.

MARK WS Barium-cadmium complex. Most powerful stabilizer available. Recommended where an exceptional degree of long-term stability is required.

MARK E Strontium-zinc laurate. Gives complete freedom from sulfide staining. Has a very low degree of toxicity.

MARK JR & MARK JO Barium-zinc complexes for the stabilization of highly filled compounds such as floor tiles, cove moldings, etc. Provide complete freedom from sulfide staining. Non-lubricating, they do not hinder processing.

MARK HH & MARK 225 Stabilizers specifically developed for vinyl asbestos flooring compounds. Give excellent long-term stability and retention of initial color. Non-lubricating, they do not hinder processing.

MARK 33, MARK 34 & MARK 35 New, non-toxic stabilizers. Give stability superior to that of any non-toxic stabilizer previously available. Withstand the high heat needed to process unplasticized vinyl. May be used in rigids as the sole stabilizer system, and give excellent stability. Approved by the Food & Drug Administration. **MARK 33** gives exceptional long-term heat stability. Recommended for pigmented or darker stocks. **MARK 34** is recommended where good initial color is required. Provides good clarity. **MARK 35** gives better initial color than Mark 33, and longer stability than Mark 34.

MARK 99 Barium-cadmium organic complex providing excellent stability and clarity at low cost for clear rigids. Eliminates problems of light stability, cross-staining and offensive odor which are encountered with tin mercaptide systems.

Plasticizers

DRAPEX 3.2 Octyl epoxy stearate. Recommended where the best possible low temperature flexibility is required. Also gives good heat and light stability, lower volatility, and greater resistance to extraction by soaps and detergents.

DRAPEX 4.4 Octyl epoxy stearate. Has a higher epoxy value than Drapex 3.2 and therefore superior heat stabilizing action.

DRAPEX 7.7 High-solvating, primary plasticizer with polymeric properties. Gives outstanding resistance to staining. Gives low volatility and excellent resistance to leaching by water, oil and other extractants.

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Leo A. Wall

National Bureau of Standards

POLYMER SCIENCE

Energetics of Polymer Decompositions

Part II

(Part I published in the SPE Journal, August 1960, page 810)

The activation energies reported in the literature for the thermal decomposition of polymers vary considerably. Discrepancies between values reported by different workers may be due to one or more factors: "purity" of initial polymer, mechanism applied to the polymer decomposition (and hence the method of treating the data), method of preparation of the polymer, molecular weight, and experimental technique.

Selected values for the activation energies, E, and pre-exponential factors, A, for the decomposition of several polymers are listed in *Table 3*. With the exception of poly(methyl methacrylate) these polymers have values which are reasonably independent of the source or method of preparation of the polymer. For the first three references the variation in the poly(methyl methacrylate) values are associated with the mechanism of initiation. End initiation appears responsible for the low values and random initiation for the high. The fourth reference reported a high value for low molecular weight polymer and a low value for high molecular weight polymer. The former polymers [29, 30, 39] were all prepared by using benzoyl peroxide or light, while the latter [40] were prepared using hydrogen peroxide and ferrous ion.

It is amply evident that both structure of end groups and molecular weight influence the decomposition of poly(methyl methacrylate). The possibility that activation energy would vary with molecular weight was pointed out also on theoretical grounds by Simha [42]. In the case of poly(alpha-methylstyrene) no such effect was observed [28]. However, in the molecular weight range studied the mechanism is mixed (see *Figure 2*), that is, the zip length is approximately equal to the D. P. The greatest difference in activation energy should occur between the situations where the zip length is much longer than the D. P. and also where it is much shorter.

In *Table 4*, activation energies and pre-exponential factors are given for a series of fluorine-containing polymers. In general, the pre-exponential factors in both *Tables 3 and 4* tend to be high, and in some cases extremely high. The high values may be a consequence of random initiation, in which case the factor should be divided by the D. P.

Assuming no transfer, one can estimate, from the data in *Figure 1* for poly(alpha-methylstyrene), a value of the rate constant for initiation, $k_i = 5.7 \times 10^{-8}$ sec^{-1} at 272°C. The activation energy for k_i is certain by no less than 65 kcal, which is the activation energy value for the overall rate of decomposition. The pre-exponential factor for k_i must then be at least 10^{19}. This value is extremely high and presumably not an artifact due to mechanism. Thus, the large pre-exponential factors for polytetrafluoroethylene and polytrifluorostyrene are not especially good indications of random initiation. Estimates of the activation energy for initiation based on data in *Tables 3 and 4*

Table 3. Activation Energies for the Decomposition of Hydrogen Polymers

Polymer	A (est) sec^{-1}	E kcal/mole	Reference
Methyl methacrylate	10^{9}-10^{16}	30-52	[39]
		32-42	[29]
		27-47	[30]
		48-32	[40]
α-methylstyrene	10^{22}	65	[28]
Styrene	10^{15}	55	[39]
Isobutylene	10^{14}	49	[39]
Propylene (linear)	10^{14}	59	[41]
Ethylene (linear)	10^{18}	72	[41]

Figure 2. Initial rates of volatilization as a function of the number-average molecular weight for polymethylmethacrylate. Points are experimental [29]; curve is theoretical.

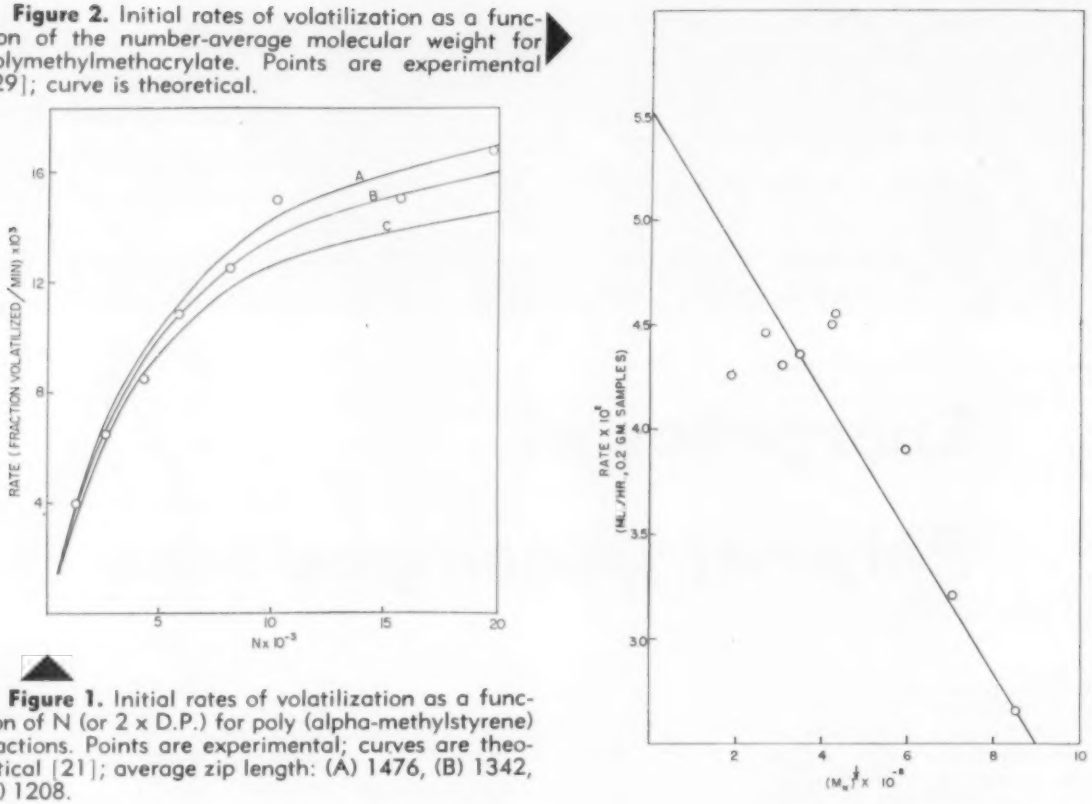


Figure 1. Initial rates of volatilization as a function of N (or 2 x D.P.) for poly (alpha-methylstyrene) fractions. Points are experimental; curves are theoretical [21]; average zip length: (A) 1476, (B) 1342, (C) 1208.

and on other available data lead to energies [28] at least high enough that initiation could be simple carbon-carbon bond dissociation. In several cases the energies appear at first sight to be too high for such dissociation. The explanation of these high values appears to be essentially the "cage effect."

Since it is unlikely that the dissociation energies of polymer bonds will ever be measured in the gas phase, the pertinent data must be deduced from condensed phase studies. Polymer decomposition studies offer the most fundamental kinetic attack on the problem. It is useful to consider the assumptions common to the gas phase situation and whether they can be carried over the condensed phase.

In *Figure 3* we depict the energy diagram for the dissociation of a molecule into two free radicals. The solid line represents the behavior of the system in the gas phase. The dissociation energy, D(R-R), which is assumed to be independent of phase, is the energy required to separate the radical fragments an infinite distance, starting from the equilibrium bond distance i.e., the distance where the energy of the system is a minimum. The chemical equilibrium is written:

$$\text{R-R} \underset{k_t}{\overset{k_i}{\rightleftarrows}} 2\text{R}.$$

where the forward reaction is the initiation step for the thermal decomposition of polymers, and the back reaction is the termination step. In general, the dissociation energy is related to the activation energies of the forward and back reaction in the following manner:

$$D(\text{R-R}) = E_i - E_t$$

A wealth of experimental and theoretical evidence supports the common practice of assuming E_t to be zero in the gas phase and hence $D(\text{R-R}) = E_i$. Now in the condensed phase "cage effects" are well known and in a viscous polymeric medium are likely to be important. An energy barrier for the combination of radicals may therefore exist, especially for large polymer radicals, and E_t in the condensed phase will be considerably greater than zero. About 20 kcal has been reported [34] for E_t in poly(methyl methacrylate) decomposition. The additional energy barrier that exists in the condensed phase is shown in *Figure 3* by the dashed curve. Both E_i and E_t are increased by the same amount. Now E_t (condensed) cannot be neglected, and it should not be surprising if E_i for a polymer decomposition is about 20 kcal greater than the dissociation energy of a carbon-carbon bond. Information on E_i and E_t requires studies such as those on the photoinduced decompositions using the rotating sector technique [44] or where post-effects are measured.

Table 4. Activation Energies for the Decomposition of Fluorocarbon Polymers

Polymer	A (est) sec^{-1}	E kcal/mole	References
Tetrafluoroethylene	10^{19}	81	[34]
α,β,β-Trifluorostyrene	10^{19}	64	[39]
Chlorotrifluoroethylene	10^{12}	50	[43]
Trifluoroethylene	10^{12}	53	[43]
1,1-Difluoroethylene	10^{10}	48	[43]

The mechanism of radical termination is also determined by these techniques. Preliminary exploration of the photo-induced decomposition of some polymers has been recently carried out in our laboratories. The typical behavior of the rate of decomposition for several polymers is shown in *Figure 4*. At an elevated temperature, usually near 200°C, where the thermal rate is negligible or barely detected, ultraviolet light causes a rise in rate which levels off or drops slightly as the polymer is consumed. When the light is turned off, the rate drops, but not instantly. Assuming the rate is proportional to the radical concentration and bimolecular termination, plots of the reciprocal of the rate should yield straight lines.

For polytrifluorochloroethylene such plots are shown in *Figure 5*, where V is the rate during the postirradiation period. The data indicate bimolecular termination far better than first order. Previous work [34] on poly(methyl methacrylate) also indicated bimolecular termination. An activation energy plot, shown in *Figure 6*, for the data of *Figure 5* yields a curious result which strongly suggests that diffusion may be complicating the mechanism at the lower temperatures. With poly (methyl methacrylate) a similar result [44] was found on the activation energy for the photodecomposition. Our Arrhenius plot for the photoinduced decomposition of polytrifluorochloroethylene gave a fairly straight line with $E_{ph} = 13$ kcal/mole.

The activation energy for thermal decomposition, E_{th}, is related to those for the elementary processes, assuming transfer is unimportant, by the relationship

$$E_{th} = \frac{E_1}{2} + E_2 - \frac{E_4}{2}$$

In photoinduced decomposition, initiation becomes independent of temperature and hence $E_{ph} = E_2 - \frac{E_4}{2}$. The activation energy from the postirradiation rates, E_{post}, plotted in *Figure 5*, is related to E_2 and E_4 thus: $E_{post} = E_4 - E_2$.

The results in *Figure 6* suggest that E_{post} at high temperatures near those where thermal decomposition occurs is nearly zero; the straight full line in *Figure 6* yields $E_{post} = -3$ kcal. For E_{th} a value of 50 kcal was obtained. From the data discussed above, we can estimate values for the processes important to polymer decomposition (see *Table 5*). It is believed that the values cited for the three polymers in *Table 5* refer to random mechanisms of initiation.

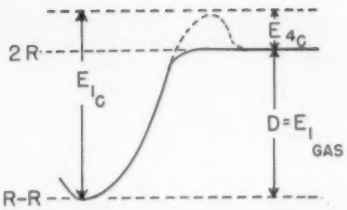


Figure 3. Dissociation Energy Diagram.

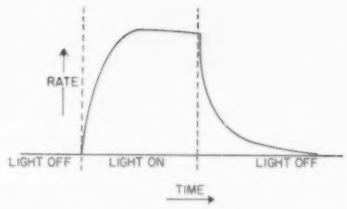


Figure 4. Photoinduced Decomposition of Polymers.

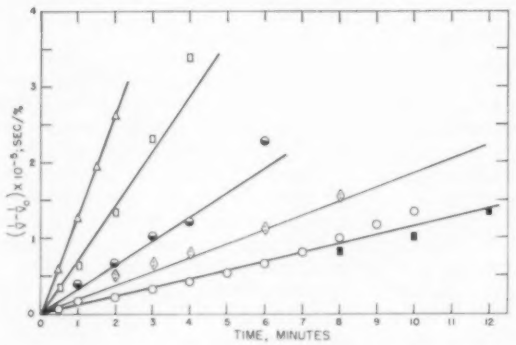


Figure 5. Decomposition of polytrifluorochloroethylene during post-irradiation period
△ 217°C
◇ 247 and 261°C
□ 225°C
○ 277°C
◒ 242°C
■ 294°C

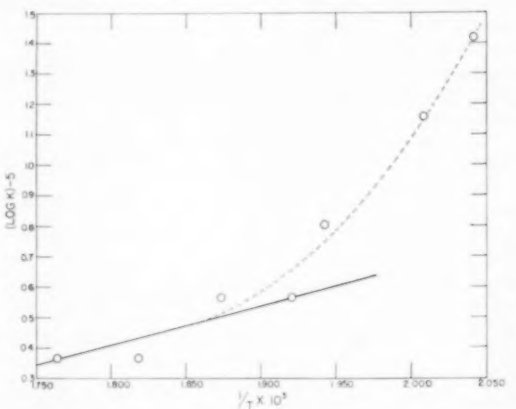


Figure 6. Arrhenius Plot for Post-Irradiation Rate of Monomer Evolution from Polytrifluorochloroethylene. K = slopes from Figure 5.

With polytrifluorochloroethylene, dissociation of carbon-chlorine bonds is the most likely initiation step. Complete validity of our treatment requires that the forward and back reactions discussed with reference to *Figure 3* involve the same type radicals, and hence we should restrict ourselves to polymers where random initiation and also bimolecular termination occurs. With end initiation there could be pictured a sort of tunnel effect where the energy barrier due to the cage effect was absent for the initiation reaction but present for the termination reaction. Also, the possibility that radicals depropagate apart can be visualized with the same consequence as mentioned for end initiation. However, it is interesting to try to extend our treatment to other polymers, despite limited data and lack of "exact knowledge" as to mechanisms of initiation. Since $2(E_{th}\text{-}E_2) = (E_1\text{-}E_4)$, then $D(R\text{-}R) = 2(E_{th}\text{-}E_2)$. The energy for depropagation E_2 is the sum of the heat of polymerization, Hp, and the activation energy for propagation in

Table 5. Energetics of Polymer Decomposition

Polymer	E_{th}	E_1	E_2	E_4
Trifluorochloroethylene	50	74	23	20
Methyl methacrylate	52	86	19	20
Alpha-methylstyrene	65	80	35	20

Table 6. Dissociation Energies of Polymers into Radicals

Polymer	D(R-R)
Ethylene	$99\text{-}2E'_s$
Propylene	$85\text{-}2E'_s$
Isobutylene	$74\text{-}2E'_s$
Tetrafluoroethylene	$70\text{-}2E'_s$
Methyl methacrylate	66
Styrene	64
Alpha-methylstyrene	60
Trifluorochloroethylene	54

polymerization E'_s and their values are available for some polymers [45]. Thus $D(R\text{-}R) = 2(E_{th}\text{-}H_p\text{-}E'_s)$. This relationship is valid regardless of the presence or absence of a cage effect.

Dissociation energies for some polymers are listed in *Table 6*. For the first four, activation energies for propagation are not available. It is likely that they are small. The size of these values suggests carbon-carbon scission in all the polymers except polytrifluorochloroethylene. Even though polyethylene produces little monomer on pyrolysis, treatment has been arbitrarily applied. It is felt that with a mechanism-producing monomer an even higher result would have been obtained. End initiation may explain low values. The value for polytetrafluoroethylene seems low. In polystyrene, where kinetics studies indicate end initiation, the listed value is not exceptionally low. In general, the results indicate that the optimum thermal stability observed with most polymers is essentially the upper limit for that polymeric structure. Greater thermal stability would require bonds with greater dissociation energies and no concomitant change in mechanism of decomposition, such as bimolecular rearrangement and exchange reactions between polymer chain. Structures with polar or ionic bonds which have high thermochemical bond strengths almost invariably have low activation energies for such bimolecular reactions.

Structure and Thermal Stability

At the present time, our knowledge of the effect of structure in hydrocarbon materials is reasonably broad. However, on completely fluorinated compounds our information is very limited but should advance rapidly in the near future. There is ample evidence of the high thermal stability of linear perfluoroaliphatic substances.

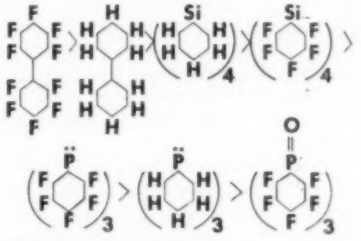
The gas phase pyrolysis of hexafluoroethane, decafluorocyclopentane, octafluoropropane, decafluoro-n-butane, and dodecafluoro-n-pentane was investigated some time ago [46]. Decomposition required temperatures of 1000°C or above. With hexafluoropropane the activation energy for decomposition was 84 kcal per mole. A low value of 51 for hexafluoroethane was suspected to be the result of heterogeneous reaction with the platinum filament used for the pyrolysis. The compounds exhibited the following order of thermal stability:

$$C_2F_6 > \text{cyclo } C_5F_{10} > C_3F_8 > \text{n-}C_4F_{10} > \text{n-}C_5F_{12}$$

Recent studies [47] on perfluoropolypropylene with an average D.P. of nine gave decomposition temperatures near 400°C, which were unexpectedly low.

Aliphatic fluorocarbons with branched structures are thus less stable than anticipated, and the thermal stabilities of high polymers based on such fluorinated structures, though possibly having desirable physical properties, are likely to be less than their hydrocarbon analogues. Although our information is extremely limited, the comparison shown in *Figure 7* illustrates the trend of the structural effect in high polymers. In the figure we compare the decomposition temperatures for related hydrocarbon and fluorocarbon polymers. The remarkable aspect is the larger range found in the fluorocarbon compared to the rather small differences between the hydrocarbon polymers. The value for a high polymer of hexafluoropropylene is, of course, a guess based on the results with the low polymer (DP=9). The failure of hexafluoropropylene to polymerize to high polymer via free radicals also suggests a low ceiling temperature and decomposition temperature.

The thermal stabilities of another series of low molecular weight substances have been recently investigated [48] in order to lay at least a partial foundation for anticipating the thermal behavior of related polymer structures. These substances, which all contain perfluoroaromatic groups, were decomposed in sealed hard-glass capillaries, and the temperatures required for decomposition were determined. The compounds are listed in order of their thermal stabilities:



For all except the last substance shown, the analogous hydrocarbon was also tested. Since these experiments were performed using glass tubes, the thermal stability of the perfluorodiphenyl was probably lowered by reaction with the glass above 500°C. The diphenyls alone completely withstood 500°C for several hours. In better containers it is believed that perfluorodiphenyl would be significantly better than diphenyl. An interesting result found is that the effect of fluorine is different for the silanes than for the phosphines.

The phosphine is improved by fluorine presumably because the electronegative atoms tend to attract the free pair of electrons on the phosphorus. In line with this is the decrease in ease with which the phosphine was oxidized to the perfluorotrisphenyl

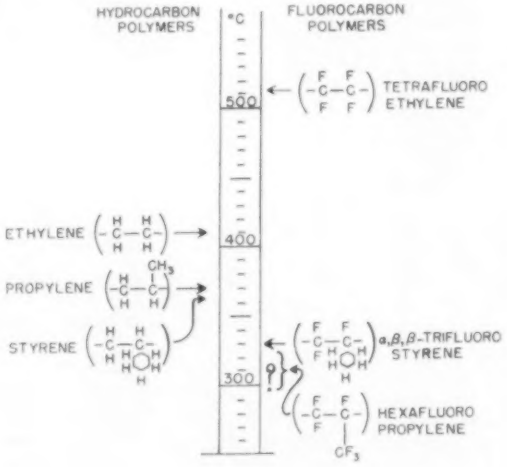


Figure 7. Decomposition Temperatures of Hydrocarbon and Fluorocarbon Polymers.

Table 7. Correlation of Radiation Crosslinking and Degradation with Heats of Polymerization and Monomer Yield on Pyrolysis

Predominance of Radiation Effect	Polymer	H_p kcal/mole	Monomer Yield Wt-%
Crosslink	(Tetrafluoroethylene)	46	100
Do.	Ethylene	22.35	0.025
Do.	Propylene	16.5	2
Do.	Methyl Acrylate	19	2
Do.	Acrylic Acid	18.5	—
Do.	Acrylonitrile	17.3	2
Do.	Styrene	17	40
Degrade	Methacrylic Acid	15.8	—
Do.	Isobutylene	12.6	20
Do.	Methacrylonitrile	15.3	85
Do.	Methyl Methacrylate	12.9	100
Do.	Alpha-Methylstyrene	8	100

phosphine oxide [48]. On the other hand, the fluorine atoms decreased the thermal stability of the silane. Otherwise, the over-all trend follows a reasonable order for single bond strengths C-C > C-Si > C-P.

Atomic Radiation of Polymers

Radiolysis of polymers is considerably less understood than pyrolysis, principally because the high energy of the radiations increases the number of possibilities for a wide variety of intermediates, ions, and excited states, as well as the radicals, normally involved in pyrolysis. Many experimental studies, principally in the gas phase, support ionic mechanisms. Nevertheless, an even larger body of evidence, principally from condensed phase studies, supports free radicals as important interminates, although, of course, the high energy radiation we are discussing always creates ionization as it deposits energy in the system. However, if the ions immediately become radicals, then the details of the effects produced depend mainly on radical mechanisms.

Comparison of heats of polymerization of polymers and their monomer yield on pyrolysis shows an interesting correlation. In *Table 7* it is seen that polymers with high heats of polymerization cross-link, while those with low heats degrade. Also, polymers with high monomer yield tend to degrade and, conversely, those with low yields, cross-link. The separation into two groups is based on whether the overall effect is predominantly cross-linking or degradation; in most cases the other process also occurs to some degree. With the exception of polytetrafluoroethylene, the correlation is not unlikely on the basis of radical mechanisms [49]. However, polytetrafluoroethylene again exhibits unique behavior. From high heats of polymerization, one anticipates cross-linking, while from high monomer yield one anticipates degradation. It seemed well established until recently [50] that this polymer degrades under radiation; however, data such as those in *Table 7* and from electron spin resonance, which identified the radical

$$(\sim\sim CF_2\dot{C}F_2\sim\sim)$$

in the irradiated polymer, did not seem compatible with degradation. It has now been found that oxygen is an important agent in the degradation observed with radiation [50]. When irradiated in vacuum at 25°C, degradation occurs, but with a rate several orders of magnitude slower than in air. On the other hand, the copolymer of tetrafluoroethylene and hexafluoropropylene shows a definite tendency to cross-link at low doses although degradation occurs at high doses of radiation.

The formation of cross-links in polyethylene is thermodynamically much more favored than in polytetrafluoroethylene; see data for reaction e and g in *Table 1*. Therefore, at best, only slow cross-linking is likely. However, cross-linked polytetrafluoroethylene would be highly desirable because of the probable improvement in physical properties which should lead to a great enhancement of its utility.

Conclusion

Presently available knowledge of thermodynamics, mechanisms, and energetics of polymer decomposition seems consistent with the proposition that carbon-carbon bonds are ruptured in the first steps of polymer decomposition. None of the polymers discussed seems to require the postulation of special weak links, and it is believed that most polymers exhibit almost, if not completely, the maximum stability to be expected for the pure substance.

The production of high-temperature-resistant polymers is an important current problem; a basis for predicting the possible solution of the problem in the form of hypothetical molecular structure is highly desirable since our resources are limited. Investigation of the thermal decomposition of model compounds appears to be the most direct means of providing this basis.

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Edited by **Dr. Irvin Wolock**
U.S. Naval Research Laboratory

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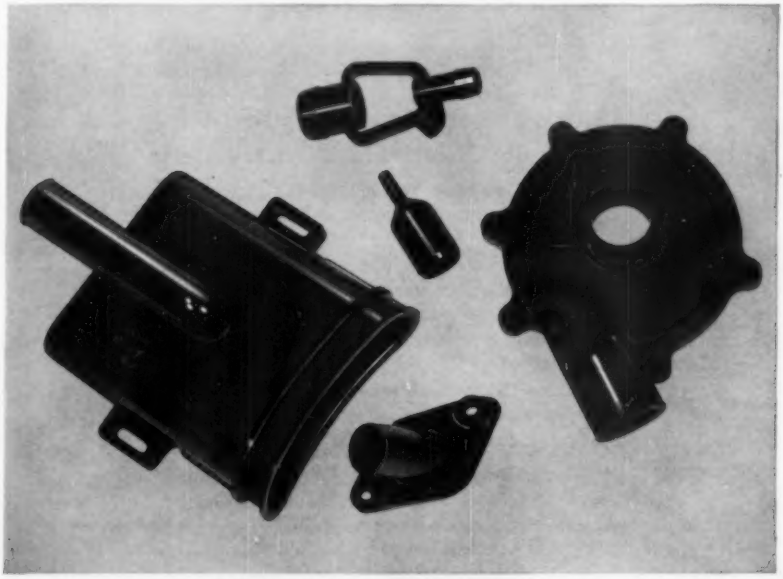

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Polypropylene . . . Its Properties and Processing Characteristics

W. L. Dunkel
and R. A. Westlund, Jr.
Enjay Chemical Co.
Market Development Division

Polypropylene . . .

- ***High temperature resistance***—
  In the range of 200 to 250°F
- ***Stress cracking***—
  Outstanding resistance
- ***Permeability***—
  Generally lower than polyethylene
- ***Injection Molding***—
  High melt index polypropylenes have spiral flows about in same range as conventional polyethylene
- ***Extrusion***—
  Can be processed by either chill roll or water bath
- ***Thermoforming***—
  Both high and low melt index resins and high and low density resins form with equal ease. In sheet formability, polypropylene has draw ratio of 1.25 to 1.

One of the most important developments in the field of high polymers, within the last ten years, has been the advent of stereospecific polymerization. Through the use of alkyl metal catalysts, ethylene can be polymerized at low temperatures and pressures to yield materials of exceptionally high density when compared to the "high pressure" type polyethylenes. The extension of this work to the stereo specific polymerization of α olefins resulted in a new class of crystalline high polymers. One of these which today is receiving much attention is, of course, polypropylene.

By its very nature, polypropylene differs quite markedly from other thermoplastic type materials which are available today. For example, it has the lowest density of present thermoplastics (0.90). It has a high molecular weight (about 300,000 $\bar{M}v$) and is highly crystalline in nature. The polymer consists essentially of three different types of polypropylene, the atactic portion, the isotactic portion and the stereoblock portion. It is the purpose of this paper to discuss these four properties more thoroughly and compare the physical properties of polypropylene with properties of other thermoplastic materials. The effects which these basic properties and other physical properties of the polymer have on its processing characteristics will also be discussed.

PHYSICAL CHARACTERISTICS OF POLYPROPYLENE

Polypropylene possesses an unique combination of desirable properties which should make it suitable for a broad range of applications. Some of these properties are: high strength, high gloss, high melting point, low density, chemical inertness, environmental stress cracking resistance, good abrasion resistance, high stiffness and low cost. These characteristics make polypropylene useful in such varied applications as injection molding, film, sheet, pipe, tubing, wire coating, extrusion coating, blow molding, monofilaments and fibers. *Table 1* compares polypropylene to the more commonly used resins.

Table 1. Polypropylene Possesses an Unique Combination of Properties

Material	Polypropylene	Acrylics	Cellulosics	Nylon	High Density Polyethylene	Polystyrene	Low Density Polyethylene
Sp. Gravity	0.89-0.92	1.18-1.19	1.09-1.22	1.09-1.14	0.93-0.96	1.04-1.65	0.92-0.94
Tensile Strength, psi	3,500-5,000	7,000-9,000	2,000-8,000	7,000-10,900	2,800-5,500	5,000-9,000	2,000-2,500
Heat Distortion Temp., °F. (66 psi)	210-230	160-195	110-235	300-360	130-175	160-210	105-180
Notched Impact, ft. lb./in. of Notch, 77°F.	0.5-2	0.4-0.5	0.4-6.0	1-3	0.5-12.0	0.5-5.0	1.5-20
Molding Temp., °F.	325-600	380-390	350-490	470-720	300-600	325-360	330-600
Molding Pressure, psi	8,000-20,000	10,000-20,000	8,000-32,000	10,000-25,000	8,000-15,000	10,000-30,000	8,000-20,000
Cost ¢/lb.	42	70	41-72	140-150	38-50	25	32-38

Table 2. Cost-Volume Relationship of Polyolefins

Material	Density	Cost, ¢/Lb.	Cost, ¢/Lb. Vol.
Polypropylene	0.900	42	37.8
Polyethylene	0.960	35	33.6
Polyethylene	0.925	33.5	31.0

Density

The low weight to volume ratio of polypropylene makes it of extreme interest to the fabricator from the standpoint of economics. Since polypropylene has the lowest density of any commercial thermoplastic, a larger volume is obtained with polypropylene than with an equal weight of other thermoplastics. Cost savings can be readily realized when polypropylene is used to replace other materials. For example, in *Table 2*, the costs of various thermoplastic materials, along with their respective densities and cost per pound-volume are given. From this, it can be seen that polypropylene with a density of 0.90 and a current market price of 42¢ a pound is competitive on a pound-volume basis with some of the newer polyethylenes having a density of 0.960 and a price of 35¢ a pound.

By the use of X-ray diffraction methods, a correlation between the crystallinity and density of polypropylene has been shown to exist. By plotting per cent crystallinity against specific volume (1/density) it can be seen that as the specific volume increases (density decreases) the crystallinity decreases. Crystallinity of the polymer is highly important in such applications as the fiber field and will be discussed later.

The density and consequently crystallinity of polypropylene can be changed by merely heating the polymer as shown in *Figure 1*. By heating polypropylene of 0.90 density (at room temperature) to 150°F., density is decreased by 0.025 units. The density decreases rapidly to a temperature of about 320°F. At this point a sharp change in density with increasing temperature is noted. This sharp change is representative of the melting point of polypropylene. This same temperature may be considered as the first order transition temperature of the material. The second order transition temperature of polypropylene is approximately −30°F.

Melt Index (Molecular Weight)

The molecular weight of polypropylene is usually determined at elevated temperatures in a high boiling solvent such as tetralin. As would be expected, the higher the molecular weight of the material the more difficult it is to process. The higher molecular weight polypropylenes are tough and tend to have low flow properties. The plastics fabricator and compounder are more familiar with melt index, which also is a measure of the flowability of the material. Because of its higher melting point, the melt index for polypropylene is usually measured under the standard ASTM conditions (2160 g.) but at a temperature of 230-250°C. (446-482°F.), rather than at the 190°C. (374°F.) temperature used for polyethylene.

Until very recently, polypropylenes having melt index values of no higher than 3 or 4 at 250°C. (482°F.) were available. Newer manufacturing techniques can produce polypropylenes with melt indexes as high as 20 or 30 at 250°C. (482°F.). These materials are much easier to mold than the low melt index or high molecular weight polypropylenes and the molded article usually possesses properties different from the low melt index material. In general, as the melt index of polypropylene is increased the impact properties of the material are decreased. However, based on our knowledge to date, we feel that high melt index polypropylenes will soon be available which have impact properties equal to or better than polypropylene of low melt index.

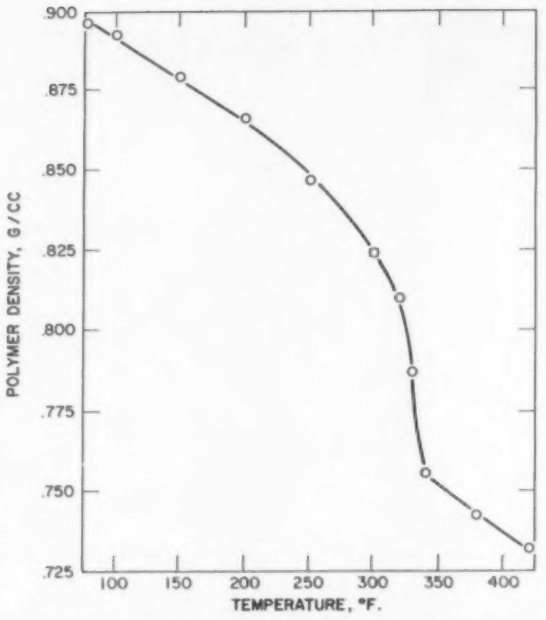

Figure 1. Polypropylene density—temperature relationship.

The effect which melt index has on the processability of polypropylene is very marked. Using the high melt index resins, articles can now be molded from polypropylene which heretofore could not be fabricated. For example, 20

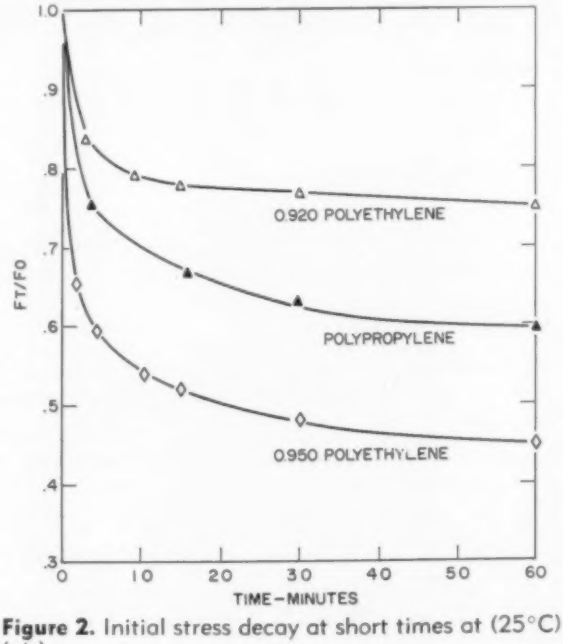

Figure 2. Initial stress decay at short times at (25°C) (air).

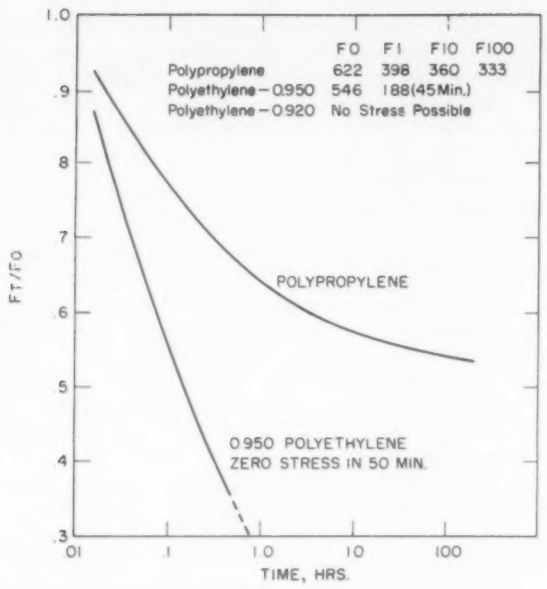

Figure 3. Stress relaxation at 194°F (air).

gallon garbage pails have been molded in a standard cycle from the high melt index resins. Articles which can be molded from low melt index polypropylene can now be made in shorter cycle times.

High Temperature Characteristics of Polypropylene

One of the outstanding features of polypropylene is its relatively high heat resistance for a polyolefin type material. Because of this, the material is finding its way into applications where temperatures in the range of 200 to 250°F. are being encountered. For the housewares manufacturer this means that he can supply materials or articles which will be resistant to the temperatures of dishwashers. It also means that where the material is to be in contact with water, which is close to the boiling point (such as in an atomizer), polypropylene can be employed with little worry regarding its durability at the higher temperatures.

Perhaps one of the best means for measuring and comparing the high temperature resistance of polypropylene with the different polyethylenes is by noting the stress decay of the material over a period of time. At test temperatures in the range of 77°F., polypropylene has a stress relaxation rate intermediate between low and high density polyethylene (*Figure 2*). This trend is apparent under conditions of equivalent initial stress, as well as with the stress equivalent to 50% of yield strength.

In this last instance, the initial load on the polypropylene and high density polyethylene is 2½ times that imposed on the low density specimen.

At elevated test temperatures as the first order transition temperature is approached, the low density polyethylene exhibits rapid stress decay. Data obtained at 90°C. (194°F.) show a rapid drop to a negligible stress (*Figure 3*). It is at the higher temperatures that polypropylene is superior to both low density and high density polyethylene polymers in stress retention. High density polyethylene after extended exposure to elevated temperatures while under stress, suffers from heat embrittlement resulting in failure of the test specimen. These observations clearly demonstrate the advantage which polypropylene has over polyethylene in applications where high temperature resistance is necessary.

Stress Cracking Characteristics of Polypropylene

Another outstanding characteristic of polypropylene is its resistance to stress cracking when immersed in various media. An accepted technique for determining environmental stress cracking tendencies involves the use of Igepal as the immersion fluid. Samples of polypropylene bent at approximately 135° and immersed in Igepal do not develop stress cracks. Samples of low density polyethylene and high density polyethylene rapidly fail under these conditions.

Stress relaxation determinations have been made in Igepal in order to give a more accurate picture of the effect of this material on these polymers at several temperatures. At 25°C. (77°F.) the high density polyethylene stress decays rapidly after 10 hours under an initial stress of 1,350 psi until sample failure occurs after 120 hours. Both low density polyethylene and polypropylene are resistant at this temperature (*Figure 4*). When tested at 40°C. (104°F.) with a slightly lower initial stress, the high density polyethylene stress cracks and fails in seven hours. Low density polyethylene and polypropylene are equivalent in their relaxation rates. However, measurements made at 70°C. (150°F.) resulted in immediate failure of the high density polyethylene and subsequent failure of the low density polyethylene after nine hours. Polypropylene survived the entire test at which point the stress relaxation rate was similar to that obtained in air.

An example of a practical case wherein the effect of stress cracking is readily apparent is as follows: Three wash basins were filled with a detergent at room temperature to a height of two inches. The filled containers were placed

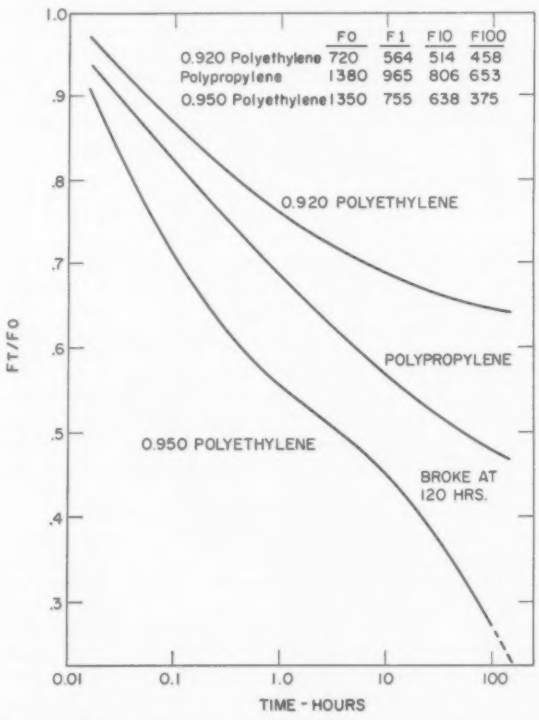

Figure 4. Stress relaxation at 77°F in Igepal.

Table 3. Permeability of Polyolefins at 75°F.[1]

Liquid	Polyethylene 0.92	Polyethylene 0.95	Polypropylene 0.896
Distilled Water	0.036	0.022	0.018
Isopropyl Alcohol	0.050	0.737	1.545
Silicone Oil	0.004	2.483	0.004
MEK	0.252	1.502	0.316
10% NaCl soluble	0.191	0.085	0.171
Linseed Oil	0.003	0.003	0.003
Mazola Oil	0.003	0.003	0
Methanol	0.318	6.188	0.145
Igepal	0.004	0.027	0.004

[1] In units of grams/4 mils/24 hours/4 in.^{2}

on ½ inch diameter steel balls and allowed to remain in this position until stress cracking took place. After 16 hours the pan made from low density polyethylene showed signs of extensive stress cracking. The pans fabricated from polypropylene exhibited no stress cracking for several hundred hours, at which time the test was discontinued. This is a practical test, since the housewife many times will place a plastic container, such as these, on top of a sharp object in the sink or on a work table.

Impact Properties of Polypropylene

The impact characteristics of polypropylene may be related to density and molecular weight. The lower density polymers, having lower isotactic contents are less stiff and have better impact properties due to their greater ability to deform under impact. The effect of molecular weight on impact properties of polypropylene is similar to that found with other polyolefins. Increasing the melt index, which corresponds to lower molecular weight, gives polymers of lower impact strength or toughness at constant resin density. At the same time a practical limitation is imposed by the lowering of flowing properties and molecular weight increases so that a balance between the impact properties and ease of processing is needed.

Since polypropylene is highly susceptible to orientation, it is not surprising to find that materials which have been oriented exhibit a much lower brittleness temperature than do those which are unoriented. This has been demonstrated both in the film and in the fiber field. For example, polypropylene which has been molded into a pad may be very stiff at 40 to 50°F. On the other hand, ropes made from monofilaments extruded from this same resin exhibit much better low temperature characteristics. Ropes made from polypropylene have been shown to be flexible at temperatures as low as — 70°F. At the same time, these ropes can be heated to room temperature and then cooled again to — 70°F. and the materials will still retain their flexibility.

Although the standard ASTM tests for impact resistance give some measure of polypropylene's susceptibility to impact, these values have not been found to correlate with end use testing of the products. Two reasons for this may be the effects which the speed of impact and cross-sectional area play. In many instances where polypropylene was thought to be ruled out because of laboratory impact tests, it has been found that the final molded article satisfactorily passed all end use tests. Thus, it behooves the fabricator to evaluate polypropylene from an end use standpoint and not only from a laboratory test method standpoint.

The impact resistance of polypropylene is highly temperature dependent. When polypropylene is compared with styrene and high impact styrene at temperatures down to 10°F., polypropylene exhibits an impact strength comparable to that of impact styrene and certainly better than regular styrene at this temperature and at all other temperatures. At temperatures between 10°F. and — 70°F., polypropylene is slightly inferior to impact styrene. However, at — 70°F. there is a cross-over and polypropylene is superior to both regular polystyrene and impact styrene at temperatures below — 70°F. Polypropylene has an impact energy of 4 ft. lbs. at — 100°F. measured on an unnotched bar and impact styrene at this temperature is the same as polystyrene, or roughly 2 ft. lbs. per in.

At higher temperatures the impact resistance of polypropylene is much greater than that of styrene, impact styrene and high density polyethylene. This was determined using a notched bar.

As mentioned earlier, the cross-sectional area upon which the impact is imposed also governs the impact resistance of polypropylene. Using the Izod-V-notch, polypropylene exhibits a constant impact resistance which appears independent of temperature. However, when a half round notched bar or an unnotched bar is employed, the impact resistance is seen to be highly temperature dependent. In relationship to polyethylene, polypropylene does not have the impact properties of the aforementioned material when measured according to ASTM tests. However, as pointed out previously, it is highly important to do end use testing with polypropylene and also consider product design if the impact properties of the material are highly important in the end product.

Where improvement in low temperature impact properties is required for specific applications blending with certain elastomers has proved effective as disclosed in U.S. patent 2,939,860. Such blends have slightly lower stiffness hardness and solvent resistance than polypropylene but the excellent resistance to environmental stress cracking is retained. These blends are finding applications where the resultant combination of properties provides the desired end production improvements.

Permeability Properties of Polypropylene

Polymeric materials, such as polypropylene, which lend themselves to bottle blowing and film forming techniques have become of great value to the packaging industry. To the manufacturer and user of such plastic containers, a knowledge of their permeability characteristics is of prime importance. Overall, polypropylene has lower permeability characteristics than polyethylene. A comparison of the permeability characteristics of polypropylene with polyethylene of both high and low density is shown in *Table 3*.

In this test, various liquids were placed in contact with a piece of 4 mil film, which had been fabricated by a flat die extrusion technique. Data in the table were obtained at 75°F. Generally speaking, the more crystalline the polymer (higher density) the better its impermeability properties. This is to be expected. Thus, where a high degree of impermeability is desirable, it is apparent that the fabricator should consider the use of the higher density polypropylene.

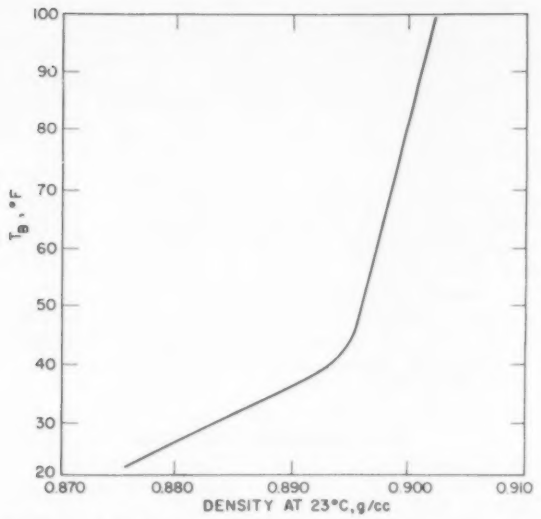

Figure 5. Effect of density on brittleness temperature.

PROCESSING OF POLYPROPYLENE

Regardless of the physical properties of a material, the usefulness of the product will be dictated by its ease of processability. Poor processability and the need for major machine modifications slow the acceptance of new materials by the fabricator. Polypropylene does not fall into this category since it basically handles as well as other thermoplastic materials in conventional processing equipment. In the majority of cases, only very minor changes in temperatures and pressures are required. At the same time very few instances have been encountered where actual changes in machine design have been required on the part of the processor.

The processability of polypropylene, especially in the injection molding field, is highly dependent upon the molecular weight (melt index) of the material. As would be expected, the lower melt index resins are fairly tough to process and require different conditions than resins having higher melt indexes. The higher melt index resins tend to process as easily as some of the intermediate high density polyethylenes. In the film field, the type of technique employed when making the film and the ultimate use of the film will dictate what range of melt indexes should be used. The same may be said in the field of extrusion coating where higher melt index resins or low melt index materials can be used. In thermoforming applications, melt index appears to have very little effect on the processing characteristics of polypropylene.

Injection Molding

Polypropylene is being used in a wide variety of injection molded items. It has good moldability, in that it tends to take to the contour of the mold very easily. Secondly, good luster and hand is obtained with polypropylene molded items. Third, cycles competitive with those of high density polyethylene and in some cases, low density polyethylene, have been obtained with polypropylene. Because of its many good characteristics, polypropylene is finding its way into many markets where before polyethylene and even nylon and butyrate were used. Injection molding of polypropylene was discussed in detail in the May 1960 issue of the SPE Journal, page 513.

Extrusion-Film

Besides the price, two characteristics of film grade resin are extremely important in determining its commercial value. The first involves the physical properties of the film, such as, clarity, haze, color, odor, and toughness. The second involves again the ease of processing of the resin in commercially available equipment.

To some extent, these two characteristics are related, since the properties of the film will depend in large measure on how the film is made. Polypropylene film can be processed by either the chill roll technique or the water bath technique at commercial rates. At the same time blown film can also be made from polypropylene. A large amount of research is presently going on in this field of application. A more complete discussion of extrusion of polypropylene film was published in Modern Plastics, by A. R. Gilden and W. J. C. McCulloch, Vol. 37, No. 11.

The manufacture of film from polypropylene is, of course, only the first step in successful utilization of this polymer for the packaging industry. The product must also be able to be heat sealed. Heat sealing ranges for polypropylene are fairly wide as shown in *Figure 7*. Polypropylene exhibits a 15 to 25°F. heat sealing range, which is adequate for most applications. Bar pressures of 2 to 20 lbs./sq. in. were used in this work. By proper control of temperature and bar pressure the seal may be varied from a complete weld to a "tack" seal which may be opened without destroying the film. In bread wrap, for example, a weld is desired for the bottom seal and tack seals at the ends of the loaf.

Over-wrapping cartons and objects with polypropylene film has been accomplished at rates comparable to that employed with polyethylene and cellophane. For example, packages have been wrapped with polypropylene film

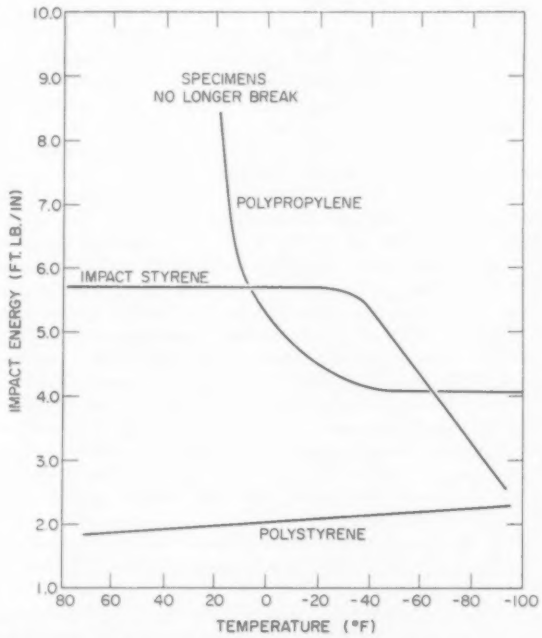

Figure 6. Polypropylene has good unnotched impact resistance.

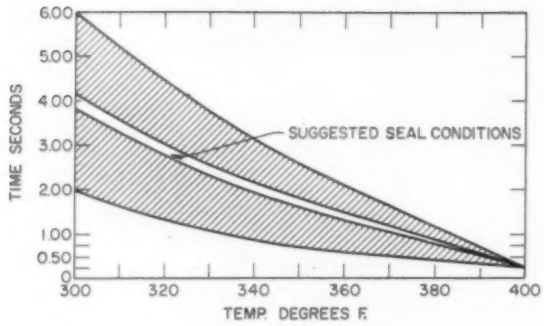

Figure 7. Heat sealing range time vs temp. at 2,10,20 p.s.i. bar press.

under ordinary factory conditions and using standard wrapping equipment at rates as high as 80 packages a minute. The limiting factor in this case was the machine, rather than the film. Polyethylene could not be wrapped at this rate on this machine. Good sealing was noted on all sides of the package.

Bags have also been made from polypropylene with only minor modification of equipment. Printing of the bags using standard techniques showed that ink susceptibility of polypropylene film was comparable to that of polyethylene after standard pretreatment. Sparkle of the printed surface with polypropylene was extraordinarily good, which would indicate that reverse printing similar to that now used with cellophane, is a "natural" with polypropylene. Polypropylene film printed in this manner shows exceptional sparkle and clarity.

Extrusion-Coating

Polypropylene has advantages over conventional polyethylene for extrusion coating in resistance to grease, moisture, heat and abrasion, as well as better gloss and stiffness.

The heat sealing properties are equivalent although slightly higher sealing temperatures are required. The distinctive flow properties of polypropylene compared to polyethylene require minor modifications in equipment and processing conditions in order to produce thin coatings at acceptable rates.

The effect of die design on coating speed before surge (uneven coating) is shown in *Table 5*.

The improved drawdown is the result of increased back pressure at the die and the internal design of the hanger die. The tear drop die produces a more uniform pressure across the die width resulting in a uniform flow profile. With the short land die, a surge pattern appears at the center of the die due to its inability to convert all the elastic responses of the polymer to viscous responses.

With high density polypropylene (> 0.900) coating speed is markedly increased by increasing chill roll temperatures. Preferred temperatures are above 150°F. Adhesion to the substrate and coating gloss are improved as chill roll temperatures are raised but curl due to shrinkage of the coating becomes more pronounced. Obviously, some compromise is then required in determining optimum chill roll temperatures.

Chill roll temperature has little or no effect on processing speeds using the lower density (< 0.900) resins. These lower density resins generally process at rates about 30% faster than high density resins under the same processing conditions. The effects of chill roll temperature on adhesion, gloss and curl are similar to those for high density resins but less pronounced.

Table 4. Film Properties

	Chill-Roll	Water-bath
Thickness, mils	1.0	1.0
Density, gms./cc.	0.8822	0.8878
Tensile (Ultimate) psi (MD)	6300	9500
Tensile (Ultimate) psi (TD)	5000	4830
Elongation, % (MD)	580	420
Elongation, % (TD)	620	770
Tear, gms./mil (Elmendorf MD)	29	11
Tear, gms./mil (Elmendorf TD)	76	~1500
Impact Strength, (Spencer) psi	2900	1520
Coefficient of friction (Egan)	0.5	0.3
Clarity (Eye Chart)—10 ft.	11	11

Film Processing Conditions

	Chill-Roll	Water-bath
Cylinder Temperature (front), °F.	525	540
Die Temperature, °F.	530	550
Resin Temperature, °F.	525	545
Film Speed, fpm	85	150-300
Chill Roll Temp., °F.	70	—
Water Bath Temp., °F.	—	70-80
Air Gap Distance, in.	¼-6*	¼-⅜

* Minimum distances usually preferred.

Other operating variables which affect processing rates with polypropylene are die position, extruder screw speed and extruder barrel temperature distribution. The poorest die positions are directly over the nip between the rubber roll and chill roll of the laminator. By moving the die to a position nearer the rubber roll and thus reducing air gap distance, coating speeds may be increased by as much as 100%. This can be explained by the highly crystalline nature of polypropylene which causes it to orient during drawdown. Reducing the air gap retards the recrystallization of the polymer during cooling. In addition, the higher melting point of polypropylene causes more rapid crystallization during drawdown than occurs with conventional polyethylene. Too small an air gap is undesirable, since this causes entrapment of air between the coating and substrate producing streaks of thinner coating in the machine direction. Optimum air gap distances are ¾" to 1". This optimum will vary slightly depending on die design with smaller values preferred for the tear drop hanger type die.

Constant barrel temperatures in the extruder show slightly higher processing rates than conditions where barrel temperature is increased from hopper section to the die. Die opening, extruder screen pack, and screw design appear to have little effect on processing speeds. Die openings between 2 and 23 mils were studied. Thinner openings are generally to be preferred to minimize the drawdown required. Heavier screen packs give higher and more uniform resin temperatures but do not affect rates. Output, as might be expected, is reduced by heavier screen packs. The extruder screws used in these studies were of the modified nylon metering type. Reducing flight depth in the metering section gives a higher and more uniform melt temperature and decreases extruder output, but does not affect coating speeds. This suggests long barrelled extruders (L/D ratios greater than 20/1) are desirable to give greater outputs of extrudate at high temperatures.

Turning to the resin properties, the two most critical properties are density and melt index. It is generally true that higher density resins are to be preferred, as in the case of film, to give the maximum chemical resistance and the best barrier properties. Unfortunately, these resins do not process as easily as resins below 0.900 in density.

For maximum processing rates it might be desirable to select the lower density resin which provides adequate barrier properties. The melt index, which is a rough measure of molecular weight, has a great effect of processing rates. As might be expected, higher melt index resins process more readily.

Preferred resins have melt index values between 10 and 20 for satisfactory processability.

Thermoforming

The high temperature properties of polypropylene compared to other low cost thermoplastics make it unique in the thermoforming field. In spite of its higher melting point, polypropylene has only slightly greater heating requirements than other commonly used thermoforming materials. The relationships between heater temperature, sheet thickness and heater time have been determined for polypropylene and a variety of other plastic materials.

Thermoforming of polypropylene sheet is not too dependent upon the melt index and density of the resin. Thus, both high and low melt index resins and high and low density resins form with equal ease.

The data presented here on the vacuum forming properties of polypropylene were obtained on an Emhart Vactrim Machine with 24 x 24 in. plattens. The machine had sandwich-type heaters with 18-900 Watt heater rods on each side and a 3 in. heater rod to sheet spacing. In order to determine the relative ease of formability of polypropylene in regard to other polyolefins, a mold was employed having nine different projections. These projections varied in ratio of height to width. Formability of the material was determined by the maximum draw ratio possible. In comparison with high density polyethylene, regular polyethylene and styrene, it was found that polypropylene is intermediate between the high impact styrene and high density polyethylene with respect to cycle time, formability and sheet sag characteristics.

Table 5. Effect of Die Design on Drawdown

Die Design	Coating Speed fpm	Coating Wt. lbs./ream	Adaptor Pressure, psi
Conventional Polyethylene— 1/16" land	25	50	100
Extended Jaw— 3/4" land	80	28	200
Tear Drop, Hanger— 1" land	150	18	550

Table 6. Effect of Melt Index on Drawdown

Melt Index, dg/m. @ 250°C. (482°F.)	Coating Speed, fpm
2	<25
6	45
9	65
15	75
26	80

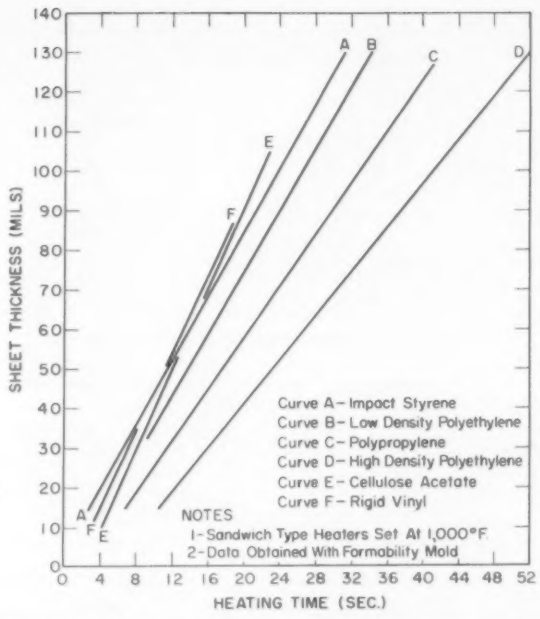
SHEET THICKNESS (MILS)
HEATING TIME (SEC.)
Curve A – Impact Styrene
Curve B – Low Density Polyethylene
Curve C – Polypropylene
Curve D – High Density Polyethylene
Curve E – Cellulose Acetate
Curve F – Rigid Vinyl
NOTES
1 - Sandwich Type Heaters Set At 1,000°F.
2 - Data Obtained With Formability Mold

Figure 8. Heating cycle varies directly with sheet thickness for a variety of thermoforming materials.

In sheet formability, polypropylene was found to have a draw ratio of 1.25 to 1. This compares with high density polyethylene with a 1 to 1 draw ratio. Impact styrene, of course, being one of the best thermoforming materials, had a draw ratio of 1.45 to 1.

Heating curves for a variety of materials used in thermoforming were also obtained using the formability mold. These curves represent the heating period required to bring a material to a temperature consistent with the material's maximum formability. The heating curves were found to be essentially linear with respect to sheet thickness. The heating period for polypropylene is slightly longer than for most other thermoforming materials, but considerably less than that of high density polyethylene (*shown in Figure 8*).

Polypropylene requires a shorter cooling period than high density polyethylene, in addition to the lesser heating requirements. The net result of this is that a production rate increase for polypropylene over high density polyethylene is obtained.

The effect of melt index on sheet sag was determined by applying a load to a small sheet so that its action during heating resembled that of a larger sheet of material. It was found that the amount of sheet sag varied in a fairly uniform manner with respect to melt index. Other thermoforming materials were positioned on this curve to determine polypropylene's relative sheet sag. Polypropylene sheet should have a maximum melt index of 2 at 250°C. (482°F.) to be equivalent to the presently acceptable impact styrene sheet. Even a lower melt index might be desirable when thermoforming polypropylene. However, sheet extrusion properties will improve with increasing melt index. Therefore, some compromise between melt index and sheet sag will be required. The effect which melt index has on sheet sag is indicated in *Figure 9*. This figure indicates that sheet sag increases only slightly to a melt index of 25 at 250°C. (482°F.). After this point, the sheet sags quite rapidly. Since this rapid sag is the result of the concentrated weight being supported by the sheet, this phenomena would not be met in practice. Therefore, the curve is considered valid only to a melt index of 25.

Table 7. Average Sheet Temperature Requirements for Various Thermoforming Materials

Material	Average Forming Temperature
Low Density Polyethylene	255°F.
High Density Polyethylene	300°F.
High Impact Styrene	315°F.
Rigid Vinyl	325°F.
Cellulose Acetate	325°F.
Polypropylene	330-350°F.

Table 8. Comparison of Marine Ropes

Fiber Type	Circumference, in.	Breaking Strength, lbs.	Wt/Ft. Lbs.	Cost per Ft. $
Manila	12	105,000	4.36	2.57
Polyester	8	103,000	2.07	7.90
Polypropylene	8½	106,000	1.70	3.91

Average sheet temperature requirements for various thermoforming materials are presented in *Table 7*.

By this same technique, polypropylene can be used in skin and bubble packages where its clarity and toughness will be an advantage over other thermoplastic materials.

Monofilaments

Polypropylene has considerable potential in the monofilament market because of its combination of high tenacity, low elongation, low creep, excellent chemical resistance, and low cost. It is currently being used commercially in such applications as filter cloths, webbing and ropes. Its advantages in the marine rope field are shown by the following data (*Table 8*).

Polypropylene is cheaper than the polyesters and lighter, making it more easily handled by shipboard personnel. It is considerably lighter than a manila line of comparable strength. In addition, it does not pick up water and become heavier in actual use.

Fiber properties are most dependent on resin crystallinity. Melt index affects processing conditions, but has much less effect on fiber properties. Monofilaments having tenacities greater than 7 grams per denier have been prepared from resins with melt indexes ranging from 1 to 30 (dg./min. @ 250°C. (482°F.)).

Table 9. Effect of Processing Variables on Tenacity

Variable	Effect, g/den.
Quench Bath Temperature	0.56
Stock Temperature	0.55
Orientation Temperature	0.98

Table 10. Relative Effectiveness of UV Absorbers

Absorber	Loss in Tenacity %
A	90
B	68
C	43
D	28
NONE	95

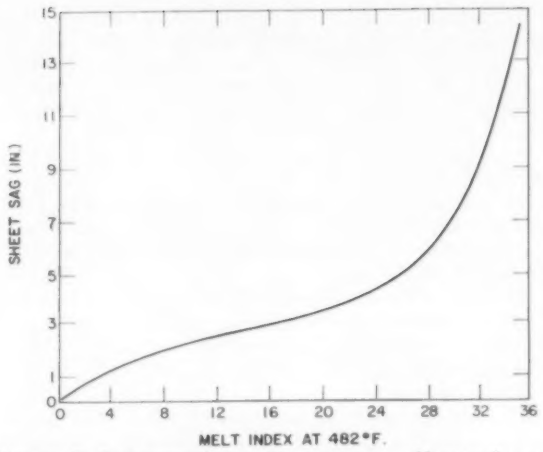

Figure 9. Polypropylene sheet sag is effectively reduced by lowering melt index.

The effect of crystallinity (density) on tenacity is very pronounced. As the density increases from 0.885 to 0.903 an increase in tenacity of 3 grams/denier is noticed. These fibers were extruded into an air bath at 80°F. and oriented at 210°F. Crystallinity does not effect knot strength to the same effect as it does tenacity.

Tenacity is also affected by processing conditions. A designed experiment to study these effects showed the following significant variables (*Table 9*).

There is also an interaction between extruder output and first godet speed. Higher tenacities are obtained using low first godet speeds at low outputs. Air gap, has no significant effect and no other inter-actions were significant under the conditions used.

Elongation is affected by most processing variables, but only within very narrow limits. The range observed was 10% to 15%, which is well within the acceptable limits for these monofilaments. This suggests that, for practical purposes, processing conditions can be selected to give maximum tenacity and the effects on elongation can be given secondary consideration.

Like other polymers, polypropylene is sensitive to ultraviolet light. Prolonged exposure of polypropylene fibers to light causes a loss in tenacity, elongation, abrasion resistance, and other desirable properties. To be satisfactory for conditions involving outdoor exposure polypropylene fibers must be compounded with an effective ultraviolet absorber which is stable through the processing steps. There are wide variations in the effectiveness of these absorbers as shown by the loss in tenacity of fibers containing small amounts of an absorber after 530 hours exposure in a fadeometer (*Table 10*).

The heat stabilizer used in polypropylene can also markedly affect ultraviolet stability. Some stabilizers can act as ultraviolet absorbers in their own right while others tend to aggrevate degradation.

The proper stabilization of monofilaments thus requires choosing the most stable base resins, incorporating the proper heat stabilizer or stabilizers, and adding the proper amount of an effective ultraviolet absorber.

Acknowledgment

The authors wish to thank the research affiliates of the Enjay Chemical Company for obtaining the data presented in this paper, as well as critique of this work.

Porous Plastic Laminates

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It is exceedingly difficult to prepare void-free, complex-shaped resin fabric laminates. Indeed, much effort has been devoted to determining experimental conditions, which would preclude the presence of voids which deleteriously affect strength (1).

In the same manner, it is difficult to deliberately prepare homogeneously porous complex-shaped laminates having interconnecting voids and a smooth-appearing surface. A porous laminate such as is envisioned here would consist of a layered fabric-resin composite in which each fabric filler is encapsulated with resin and has unabridged voids between the fibers.

This laboratory faced the problem of preparing such homogeneously porous laminates when it became desirable to fabricate laminated plastic arm prostheses which would permit removal of perspiration from the stumps of arm amputees.

The purpose of this paper is to describe the method developed for the preparation of porous laminates and to delineate their properties.

Experimental

Porous Laminate Fabrication.

Cylindrical laminates (diameter 2.93″x6.5″ length) were prepared over aluminum mandrels in the following manner:

First, a polyvinyl alcohol film was tailored to the shape of a truncated cone (PVA bag) with a base diameter slightly larger than the diameter of the cylinder and the apex diameter approximately 2 inches smaller than the cylinder diameter. The PVA bag was pulled snugly over the aluminum mandrel which had been coated with glycerine. Three layers of nylon stockinet, 2½ inches wide,* were pulled over the mandrel and tied at each end. Another PVA bag was prepared and pulled snugly over the layup and tied at the bottom. This PVA bag was made long enough to extend approximately 1 to 2 feet above the mandrel. A liminating resin mixture consisting of the following ingredients was compounded:

Resin ERL (epoxy) 2795	80 g.
Hardener (amine type) ERL 2793	20 g.
Diluent	variable

(Note: Diluent was added to the resin before the hardener.)

The resin mixture was poured into the top of the PVA bag and allowed to impregnate the stockinet by squeezing the top of the PVA bag. Further impregnation was achieved by milking the resin downward and by "stringing" with downward motions of a string along the length of the layup. Finally, the tapered PVA bag was pulled down and stretched tightly over the layup. The impregnated laminate was allowed to remain at room temperature (80°F ± 5°F) for a predetermined time. This precure time varied from 1 to 3 hours. During this time, gelling and partial curing occurred. At the end of this precure period, the outer PVA bag was removed. The surface of the laminate was wiped with a damp paper towel, using gentle strokes to flatten the fabric hairs back into the laminate. The layup was then placed in a circulating-air oven at 100°C for 2 hours, removed from the oven and permitted to cool. The laminate was then separated from the mandrel and cut to length for porosity and mechanical properties testing.

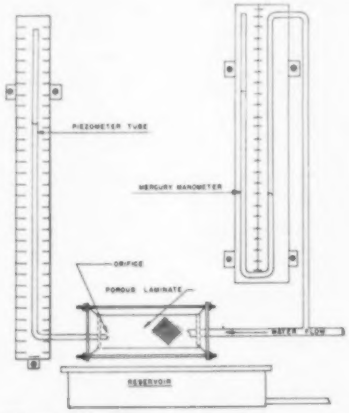

Figure 1. Porosity testing apparatus. Water flow at varying pressure heads was determined by measuring the amount of water collected in the calibrated reservoir in a given time period

Porosity Testing. To determine the relative porosity of different laminates, water flow rates at equal pressure heads were measured in the apparatus shown in *Figure 1*. The water flow at varying pressure heads was determined by measuring the amount of water collected in the calibrated reservoir in a given time period measured with a stopwatch.

* Eagle Beef Cloth Co., Brooklyn, N. Y.

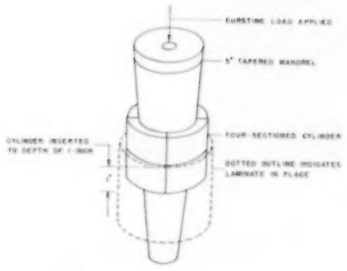

Figure 2. Schematic drawing of testing set up

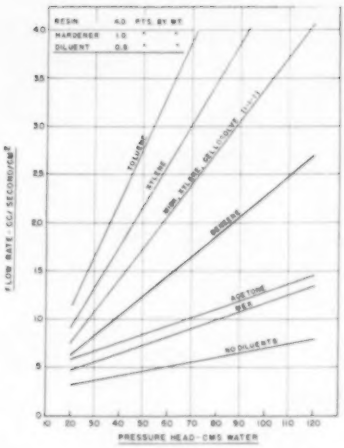

Figure 3. Effect of various diluents on flow rate through porous laminates

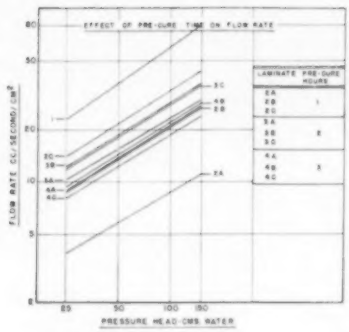

Figure 4. Effect of pre-cure time on flow rate

The term "effective porosity" was defined as the ratio of the flow rate through the laminate to the flow rate through the stockinet alone.

Mechanical Properties. (a) Impact Resistance. Impact resistance was determined using an apparatus containing a graduated tube for guidance of a dropping weight and a sample mounting. The test was carried out by dropping a 1-lb. weight onto the sample from heights, in increments of 3 inches, until failure. Heights to cause initial crazing across the laminate, cracking and collapse were noted and the results reported in inch/pounds, e.g., the height of the drop multiplied by the weight of the object. The sample was a half cylinder obtained by cutting the cylinder along its longitudinal axis. The weight was dropped on the convex surface of the hemicylinder.

(b) Bursting Load. A schematic of the testing setup is shown in *Figure 2*. The load is applied by a Baldwin Universal Tester at a crosshead speed of 0.2 in/min onto a 5°-tapered mandrel which expands a four-sectional cylinder in a direction perpendicular to the long axis of the laminate. The force required to cause the laminate to fail was recorded.

(c) Bearing Strength. The bearing strength was determined according to the procedure described in ASTM D953-54.

(d) Compression Test. Buckling stress and strain were determined by compressing a 3-inch long cylindrical laminate using the Baldwin Universal Tester. The loads were applied at a crosshead speed of 0.1 inch/minute.

Results

Figure 3 illustrates the flow rate curves obtained with a series of laminates prepared, using different diluents. One is immediately aware of the wide spread of flow rates of the different diluents as compared to the flow rate of the laminate with no diluent. Compare, for example, the flow rate at 50 cm pressure head of the samples made with toluene and those made without diluent. The samples made with toluene had a flow rate of 2.8 cc/sec, while the no-diluent laminate had a flow rate of only 0.45 cc/sec.

The order of effectiveness of solvents used in producing porous laminates is summarized in *Table 1*.
It may be seen that toluene was the most effective diluent and MEK and acetone were the least effective. Within the range of pressure heads tested, the plots may be described by an equation of the filtration type (2).

$$\frac{(dv)}{(d\theta)}\,\frac{1}{A} = \frac{P}{WR} + K$$

where V is the volume of water (cc/sec.) collected up to time, T,

θ is the time, in seconds
A the total area, in cm²
W the viscosity, centipoise
P the pressure drop across the laminate, in cm H_2O, and
R the resistance of the laminate to water flow.

From the slopes of the lines in *Figure 1*, listed in column 2, *Table 1*, in c.g.s. units, the resistance of each laminate to water flow has been calculated. The data indicate that the porous laminates prepared with no diluent gave approximately 100 times the resistance of a laminate made with toluene as solvent.

Because of the low toxicity and nonflammability of trichloroethylene, it was decided to prepare a series of laminates using this diluent. (*Figure 4* summarizes some typical water flow curves obtained.) The data are plotted on log log paper in order to make possible the comparison between the very high porosity of stockinet alone (curve #1) and the porous laminates. It is observed that very high porosities were obtained; for example, curve 2C has a flow rate of 33 cc/sec at a pressure head of 100 cm. Furthermore, a fair duplication of laminates was obtained; this may be observed by comparing curves 3A, 3B and 3C. For these reasons it was decided to study the system using trichloroethylene as diluent in further detail. To aid in analyzing the data, the term "percent effective" porosity was devised. This is defined as the ratio of average flow rate through a laminate to average flow rate through the stockinet alone. The flow rates at 15, 30 and 45 inches were averaged to give the average flow rate.

Table 1.

Solvent	Slope $\frac{cc/sec/cm^2}{cm}$	R*
Toluene	0.567	1.75
Xylene	0.415	2.41
MIBK-Acetone	0.323	3.09
Benzene	0.0197	50.6
Acetone	0.0090	111
MEK	0.0090	111
No diluent	0.0049	204

* $R = \frac{1}{W} \times \frac{1}{\text{Slope}}$

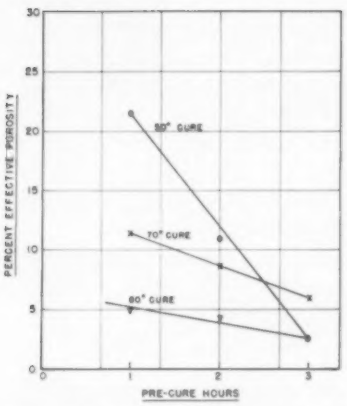

Figure 5. Effect of pre-cure time on effective porosity Resin ERL 2795 Hardener ERL 2793 Diluent Trichloroethylene 1.08

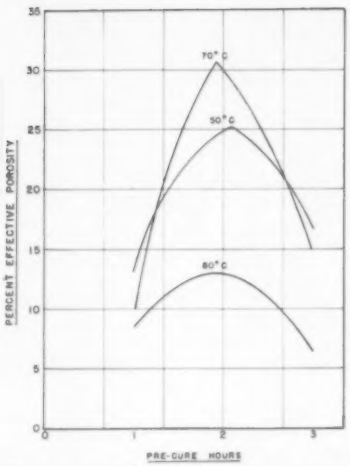

Figure 6. Effect of pre-cure time on effective porosity Resin 4.0 parts by weight Hardener 1.0 parts by weight Diluent Trichloroethylene 1.295 parts by weight

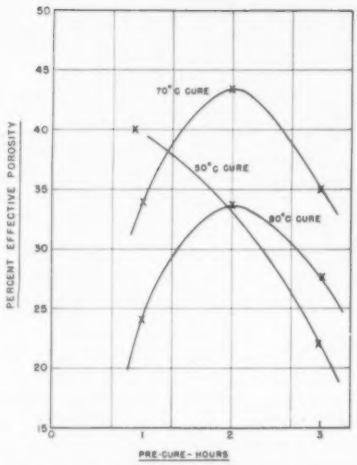

Figure 7. Effect of pre-cure time on effective porosity Resin ERL 2795 4 Hardener ERL 2793 1 Diluent Trichloroethylene 1.73

Figures 5, 6 and 7 summarize the effect of precure times on percent effective porosity for a given cure of varying concentrations of diluents. It is observed that at 15% (1.08 by wt.) by volume of diluent the shorter precure times give higher effective porosities, with the curing temperature of 50°C exhibiting the highest porosity. At the higher concentrations of diluent, a maximum in the percent effective porosity seems to occur at a precure time of 2 hours and a cure temperature of 70°C. It may also be noted from these curves that the higher the concentration of diluent the greater the effective porosity (*Figures 6 and 7*). The results show that for greater porosities a precure time of 2 hours and a final cure at 70°C seem indicated.

To determine the relationship between percent effective porosity and percent voids, the percent voids were calculated as follows: It was assumed that the weight of the nonporous laminate was directly proportional to the thickness of a nonporous laminate. A nonporous laminate of weight W_{np} has a wall thickness L_{np}. Therefore, a nonporous laminate of thickness L_p weight

$$\frac{L_p}{L_{np}} \times W_{np}$$

The quotient of the actual weight of a porous laminate W_p and the quantity $\frac{L_p}{L_{np}} \times W_{np}$ is a measure of the amount of material in the porous laminate. Therefore, the percent material in the porous laminate is $\frac{W_p}{\frac{L_p \times W_{np}}{L_{np}}} \times 100$. The percent voids is, therefore,

$$100 - \frac{W_p}{\frac{L_p \times W_{np}}{L_{np}}} \times 100.$$

Substituting the average weights and thicknesses of nonporous laminates, the expression for percent voids reduces to

$$\% \text{ voids} = 100 - \frac{W_p}{1.22 L_p} \times 100.$$

Figure 8 summarizes the relationship between the percent voids and percent effective porosity. Up to approximately 30% voids the laminate is rather ineffectual in permitting flow. However, at this point the slope of the curve changes sharply and a small increase in the number of voids causes a large increase in effective porosity. Interestingly enough, the curve extrapolates to a value of approximately 74% voids at 100% effective porosity. This compares to the calculated value of the percent voids (from density measurements) in the stockinet alone of approximately 72 per cent. These data seem to indicate that at low percent void contents the voids are discrete and not interconnecting.

Two main factors contribute to the porosity of porous laminates. The greater factor is the presence of a diluent. The removal of the diluent by evaporation leaves many voided areas which contribute greatly to the over-all porosity of the laminate. Another, less obvious factor was revealed by the preparation of a porous laminate even without a solvent. This indicates that the other contributing factor lies in the removal of the PVA bag after a certain precure time. If the bag is not removed, a nonporous laminate results.

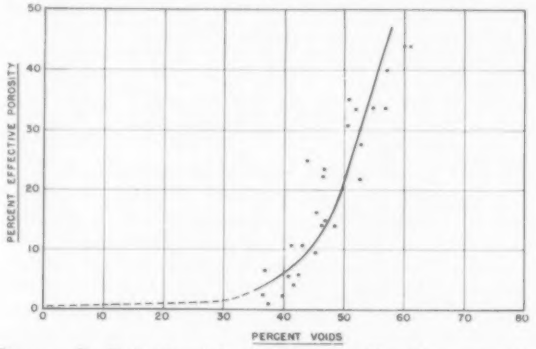

Figure 8. Relationship between effective porosity and percent voids
Resin ERL 2795
Hardener 2793
Diluent Trichloroethylene

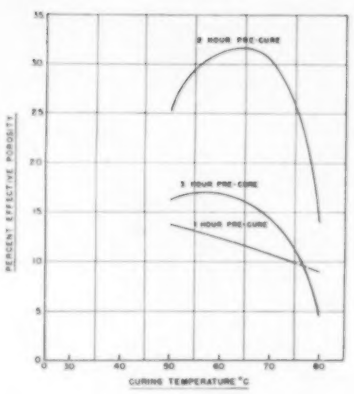

Figure 9. Effect of Cure Temperature on Effective Porosity
Resin ERL 2795
Hardener ERL 2793
Diluent Trichloro-ethylene

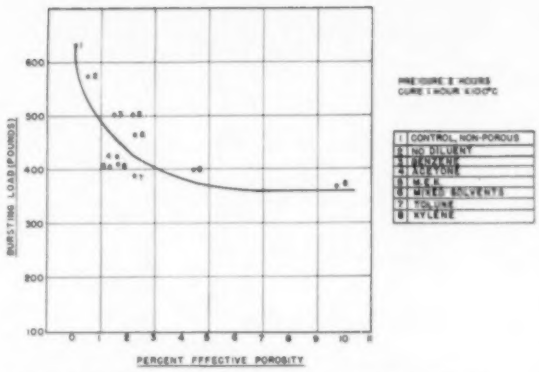

Figure 10. Effect of porosity on bursting load
Resin ERL 2795
Hardener ERL 2793
Diluent Varied

Removal of the PVA bag results in an expansion of the layup. It is believed that the expansion permits overcoming the cohesive forces between liquid resin particles and, thereby, minimizing bridging in the stockinet interstices. Ideally, if the adhesive forces between the stockinet fibers and resin are much greater than the cohesive forces in the liquid, the cured laminate would consist only of coated stockinet fibers with minimum bridging between the fibers. Steps taken to lower the cohesive forces between the resin molecules should aid in enhancing porosity. Solvents may perform this function.

There are however, limitations imposed on the physical characteristics of the solvent diluent used. First, the boiling point of the solvent is an important consideration. If a diluent was chosen whose boiling point was too low, the diluent could be driven off too rapidly after bag removal, permitting the thickened resin to flow into and remain in the voids before the laminates were cured and thus result in low porosity. It may be noted in *Figure 3* that when the curing temperature was 100°C, those laminates made with acetone, MEK, and lower-boiling solvents gave laminates with low porosity, whereas xylene and toluene solvents, whose boiling points are higher than the curing temperature, gave highly porous laminates. Similar results are obtainable when using trichloroethylene as a diluent. These data are summarized in *Figure 9*, in which the final curing temperature was varied between 50°C and 80°C for a series of laminates prepared at different precure times. In all cases, as the curing temperature approached the boiling point, the average laminate porosity decreased. It is felt that for optimum porosity some curing temperature somewhat lower than the boiling point of the diluent should be chosen. Another limitation upon the solvent is imposed by epoxy resin itself. Since the cures of the epoxies are ionic in nature, the dielectric constant of the solvent chosen may be of importance and affect the rate of cure. Too rapid a cure rate may permit solidification of the resin during the precure period (prior to the removal of the PVA bag) and thereby produce a laminate whose porosity is low.

Finally, a word should be said concerning the effect of ambient temperature and humidity on laminate porosity. *Table 2* summarizes the recommended precuring conditions at a series of ambient temperatures and at a series of humidity ranges. These data are based on the porosity of laminates prepared under the conditions specified. For a given set of specified conditions, laminates of equivalent porosities should result. From *Table 2* it may be concluded that as the ambient temperature is increased, the precure time at all humidity ranges should be decreased. In the same manner, as the ambient humidity range is increased, the rate of cure is accelerated. Thus higher humidities require shorter precure times. To prepare laminates of optimum porosity, therefore, it is necessary to specify a precure time for each temperature-humidity range.

Mechanical Properties. The mechanical properties of the porous laminates were studied. *Figure 10* summarizes the effect of percent effective porosity on bursting load. It is observed that there is initially a rapid drop off in resistance to bursting load as a function of percent effective porosity. However, the curve flattens rapidly after 5% effective porosity. Data on ultimate compressive stress and bearing stress as a function of percent effective porosity are summarized in *Figures 11 and 12*. The shapes of these curves are similar to that of the bursting load as a function of percent effective porosity. There is initially a large drop, followed by a levelling-off process.

The curves for impact resistance versus percent effective porosity are summarized in *Figure 13* for the toluene series, and more complete data for the trichloroethylene series are given in *Figure 14*.

It can be seen that the resistance to initial damage from impact seems to increase with effective porosity, and then decrease. The same behavior is observed in the case of the trichloroethylene series for resistance to initial damage. Apparently at the lighter loadings, the porous laminates have the ability to deform and absorb the impact energy. Once the initial damage has occurred, however, the ability to

Table 2.

Room Temp. °F	Precure Time at Low Humidity at 20-40% (Minutes)	Precure Time at Intermed. Humidity 40-60% (Minutes)	Precure Time at High Humidity 60-80% (Minutes)
60	150	135	120
65	135	120	110
70	125	110	100
75	110	100	90
80	100	90	80
85	85	75	70
90	75	65	60
95	65	55	50
100	50	45	40

Precure time starts as soon as the resin has been mixed.

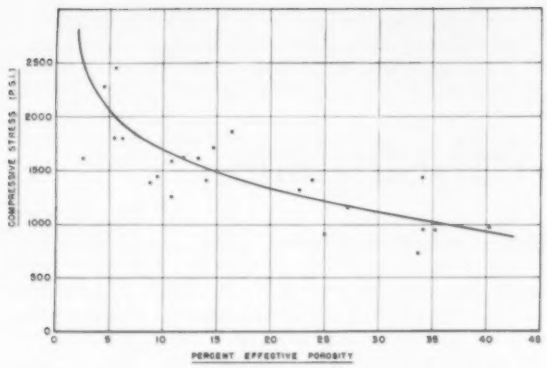

Figure 11. Compression stress as a function of effective porosity
Resin ERL 2795
Hardener ERL 2793
Diluent Trichloroethylene

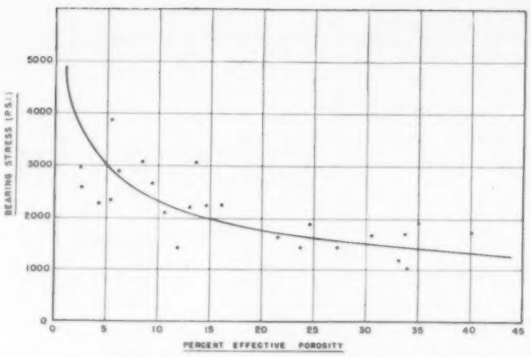

Figure 12. Bearing stress as a function of effective porosity
Resin ERL 2795
Hardener ERL 2793
Diluent Trichloroethylene

resist further loadings decreases as a function of percent effective porosity. This effect is shown by the upper curve in the trichloroethylene series in *Figure 14*.

Summary

A method has been devised for the preparation of porous laminates. The rate of flow of water through the laminates and the mechanical properties of the laminates have been determined. The flow rate of water through the laminate, at least in the pressure range measured, appears to be proportional to the pressure head. The factors found to be important in affecting the porosity of the laminates are concentration of the diluent, boiling point of the diluent relative to final curing temperature, precure time before removal of the PVA bag, and ambient temperature and humidity. These factors were systematically investigated and optimum conditions established for preparing the porous laminates. A mechanism for the formation of porous laminates is presented.

The mechanical properties of porous laminates as a function of porosity have been measured. In general, bearing strength, bursting strength, and compressive strength initially decrease rapidly with increasing porosity, and then show a leveling off. Resistance to initial impact stresses seems to increase with increasing porosity to a maximum, and then decrease. It is felt that because of the presence of pores, the laminate may yield and be able to absorb greater impact strength than a nonporous laminate. However, once initial damage has occurred, the resistance to further impact decreases with increasing porosity.

Although the method described for the preparation of porous laminates was successful, there appear to be several shortcomings to the present system. These are the effect of ambient humidity and temperature on laminate porosity, and the ribbed surface of the laminate due to the ribbed structure of the stockinet material used. In subsequent work, the effect of ambient temperature and humidity was minimized and a study of knit stockinets of varying denier resulted in very smooth-surfaced porous laminates.

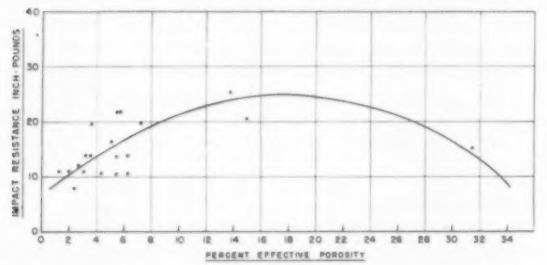

Figure 13. Effect of porosity on impact resistance Resin ERL 2795 Hardener ERL 2793 Diluent Toluene

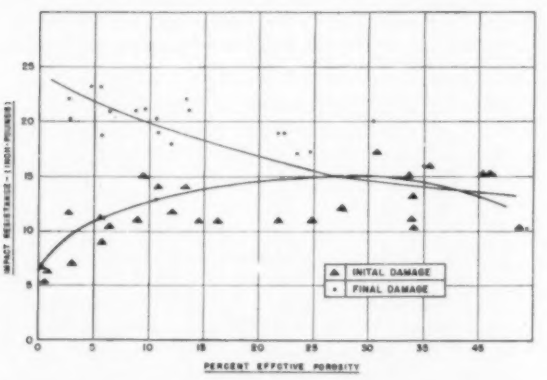

Figure 14. Impact resistance as a function of effective porosity Resin ERL 2795 Hardener ERL 2793 Diluent Trichloroethylene

Acknowledgment

It is a pleasure to acknowledge the assistance of John W. Hodge, Jr., in carrying out many of the physical measurements recorded.

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2. Perry, J. H., *Chemical Engineers Handbook*, Ed. 2, McGraw-Hill Book Co., 1941; Filtration, p. 1653

This article was adapted from a paper presented before the Division on Paint, Plastics and Printing Ink Chemistry, Am. Chem. Soc. meeting, Atlantic City, N. J., September 13-18, 1959.

Coloring Linear Polyethylene

P. E. Campbell, R. J. Martinovich and T. V. Gay

Phillips Chemical Co.

Three simple tests to tell you which pigments you can use:

- *Migration test*
- *Fading due to Ultraviolet light*
- *Heat stability*

Considerable knowledge on the coloring of low density polyethylene has been gained over the past several years. When MARLEX* polyolefins became available, this knowledge was applied to these new resins. Due to the differences in properties of the polyethylene resins, some minor modifications were necessary. A consideration of the pigments employed and their effect on the physical, chemical and electrical properties of linear polyethylene will point out the areas of special significance.

Methods of Coloring

There are three widely used coloring techniques (1) (Diagram). They are: A) Concentrate let down or dry pigment-resin blending by banbury milling or extrusion prior to final processing; B) Concentrate-resin blend, molded or extruded directly into the finished product and; C) Dry blending of resin and colorant and injection molding or extrusion into the finished product. Methods B and C are probably the most widely used. Method C is very popular in general purpose injection molding while Method A is preferred in those applications where dispersion of pigment is critical, such as in fiber, film or wire coating.

The initial blending operation of resin pellets and dry pigment is very important and can to a large degree determine the dispersion in the finished product, especially when dry blending and injection molding.

Small amounts of pigment (as high as 1%) can be adequately dispersed with the resin without the use of a wetting agent. The electrostatic charge on the resin caused by the tumbling action is sufficient to prevent the separation of the pigment from the resin. With larger amounts of pigment a wetting agent is necessary. Mineral oil is an excellent wetting agent since in low concentrations (0.02% to 0.05%) it has little effect on the physical properties, except for a slight decrease in melt viscosity. Higher concentrations of mineral oil give a grey cast to the resin making it extremely difficult to obtain a bright white color or any light pastel. There is also some evidence that the weatherability of the compounded resin may be adversely affected.

Stearates are also sometimes used to improve the dispersing characteristics of pigments. They are quite effective and when used with titanium dioxide actually increase the white appearance of the resin. In concentrations of <1% their affect on most of the physical properties is negligible. There is, however, an increase in melt flow which can be ascribed to the lubricating action of the stearate. The affect of even a low concentration of stearate on the stress crack resistance of linear polyethylene is not yet clearly defined and their use should be approached with extreme caution.

A typical blending operation for either dry pigment or concentrate would consist of tumbling the wetting agent (0.02% to 0.05%) for 5-10 minutes, adding the pigment and other additives and subsequently mixing for an additional 10-30 minutes. Excessive tumbling should be avoided since this may cause agglomeration of the pigment. In addition, the tumbling should be done just prior to use since stratification of the concentration or dry pigment and resin may occur on standing.

Injection Molding

A number of variables must be properly controlled during injection molding if maximum color dispersion is to be achieved (2).

In general, reducing the pellet size, pinpoint gates, low melt index resin and a Venturi type dispersion plug all aid in improving the dispersion of the pigment. Many of these variables are controlled by the part design and therefore it is not possible to modify them for optimum pigment dispersion.

Three routes to the coloring of linear polyethylene

* A trademark for Phillips' family of olefin polymers.

The type and design of the dispersion plug can be changed to significantly improve dispersion regardless of the design features of the mold. The Venturi type dispersion plug as proposed by The Ferro Corporation is superior to the other types now available, including the polyliner, pineapple, ball bearing and two plate plug and should be used when coloring by injection molding.

Extrusion

Several factors must be considered when coloring by extrusion is to be done. The use of single screw extruders, equipped with standard polyethylene metering type screws is not normally recommended for coloring linear polyethylene starting with a resin-pigment blend, especially for quality colored parts. If a single screw extruder is the only equipment available, mixing of resin and pigment can be improved by special compounding screws. These screws, which usually contain some type of a masticating section some place along its length, are readily available and do an excellent job. Special compounding extruders are also available, such as twin screw machines, or the Ko-Kneader, manufactured in Switzerland.

If low extruder temperatures can be maintained (<400°F) during the production of finished parts, the coloring and extrusion of finished parts can be accomplished at the same time. The equipment and conditions listed were used to prepare colored 125 mil sheet with adequate dispersion for most uses. Changing any of the extrusion variables would have a definite effect on dispersion. As the thickness of the sheet is decreased the pigment dispersion becomes more critical. Therefore colored sheet, 60 mils or less in thickness, should be extruded from precompounded stock or with the aid of a special mixing screw.

Three Screening Tests for Determining What Pigments May be Used.

- *Color Migration*;

  A compression molded sheet of the colored resin is placed in contact with filter paper and a sample of plasticized polyvinyl chloride. (Geon 101 plus 100 parts DOP). This sandwich is placed in an oven for 72 hours at a temperature of 50°C. At the end of this period if the filter paper and polyvinyl chloride sample are free from color, the colorant is acceptable.

- *Fading Due to Ultraviolet Light*;

  A molded sample of the colored resin is exposed in an Atlas Fade-ometer for a period of 200 hours. The colorant is acceptable if no color change occurs as observed by the naked eye.

- *Heat Stability*;

  A compression molded sample of the colored resin (2"x3") is enclosed in household aluminum foil, the foil wrapped tightly about the sample to exclude as much air as possible. This wrapped sample is then placed in a circulating air oven at 500°F for 30 minutes. If the sample retains its original color (as observed by the naked eye) it is acceptable.

Table 1. Pigments Suitable For Linear Polyethylene

Black	Carbon
Red, Orange, Yellow	Cadmium (Selenide, Sulfide and Lithopones), Mercury-Cadmium
Blue	Phthalocyanine, Ultramarine, Cobalt
Green	Phthalocyanine
Brown	Iron Oxide (Calcined)
White	Titanium Dioxide (Antase, Rutile)

Conditions For Extrusion of 125 Mil Colored Sheet From a Dry Pigment-Resin Blend

Pigment:	1% Cadmium Selenide
Method of Addition:	Dry Blended (no wetting agent)
Resin:	MARLEX 6000, Type 2
Extruder:	2½" NRM with an L/D ratio of 20:1
Screw:	Standard Polyethylene Metering Type
Screen Pack:	20, 80 mesh
Screw Speed:	71 rpm
Cylinder Temp., °F.:	
Zone 1	310
Zone 2	320
Zone 3	330
Zone 4	340
Head Temp., °F.:	340
Head Pressure, lbs.:	1100
Die Temp., °F.:	340

Selection of Pigments

There is an adequate number of pigment types sufficiently stable to the screening tests given here to give a wide range of colors. *Table 1* lists those pigments found suitable for Phillips Chemical Company's polyolefins and other linear polyethylenes. The range of color of dyes available for colored transparent films is limited.

From time to time there are reports of certain pigments causing polymer degradation and odor development (3). Although we have examined combinations of pigments which supposedly cause these effects we have not been able to substantiate these results. One serious difficulty, however, has been noted—warpage. This warpage may occur in injection molded flat parts produced from molds which are inadequately cooled. Since a 1% concentration of phthalocyanine blue makes a normally simple operation, very difficult, injection molding of flat parts containing this pigment would be extremely difficult. The warpage seems to occur even in color formulations containing only a small proportion of this pigment.

Evidence to support the theory that there may be a reaction between the pigment and resin was gained in thermal stress cracking tests at 212°F. Utilizing the Bell Laboratory bent strip test all of the pigments tested had an F50 value of greater than 500 hours except phthalocyanine blue. The F50 value for this sample was four hours.

These results do not mean that this pigment should be avoided for use in linear polyethylene but it does mean it should be used with caution in concentrations as high as 1% and especially in those applications where thermal stress cracking resistance is important. The environmental stress cracking resistance of this sample was slightly lower than the unpigmented control but still adequate. This degradation effect has not been observed with phthalocyanine green.

Some discoloration of molded parts during processing or in subsequent use has been observed. In some cases this

Table 2. Recommended Antioxidants For Pigmented Linear Polyethylene

Colors	Antioxidant	Concentration
Dark Colors	2,6, ditertiary butyl-p-cresol or 4,4'-thiobis-(6-tert.-butyl-m-cresol)	0.05% or less
Whites and all Pastels	2,6, ditertiary butyl-p-cresol	0.02% or less
Black (for maximum protection)	4,4'-thiobis-(6-tert.-butyl-m-cresol)	0.10% or less

color change has been caused by pigment degradation. Frequently, however, this effect is due to a color change in the antioxidant. *Table 2* gives the antioxidants and concentration depending on the color requirements.

Properties

Not only must a pigment pass the screening tests described but it must have little or no affect on the properties of the resin. However, because of the importance of electrical properties, weld strength in injection molding and weatherability, these are discussed in detail.

A. Electrical Properties: *Table 3* lists the electrical properties of some pigmented samples. It is evident that at a 1% pigment loading there is little or no effect in the frequency range of 1 Kc to 1 Mc. Carbon black which is added to polyethylene wire compounds in amounts as high as 2.5 to 3.0% causes a ten-fold increase in the dissipation factor at 1 kilocycle and 1 megacycle. The dielectric constant is also significantly affected. The slight increase in dissipation factor for the sample containing phthalocyanine green may be due to the poor dispersion of the pigment.

B. Weld Strength: The weld line is defined as a mark on a molded plastics piece made by the meeting of two flow fronts during the molding operations (4). It can be a source of failure in improperly molded pieces.

To determine the effect of pigment and molding conditions on the weld strength, a turquoise pigment was added by four different methods and samples molded at four different temperatures. The pigment was added by: a) mill blending with dry pigment; b) dry blending with pigment; c) mill blending with concentrate and; d) dry blending with concentrate. Cylinder temperatures used were 325°F, 400°F, 475°F, and 550°F. A test specimen gated at each end, designed to test weld strength, was used. The results at a cylinder temperature of 475°F are representative (*Table 4*). This data shows:

1. For certain molding configurations that develop sharp weld lines, the use of dry blended color concentrates should not be used. If it is necessary to use a color concentrate, it should be let down by milling or extrusion prior to molding.
2. The weld strength of a properly pigmented sample is no lower than the weld strength of the unpigmented resin and is 5% to 15% lower than the tensile strength of the base resin.
3. In the range of 375°F to 550°F cylinder temperature was not important in this study. In more difficult to fill molds, however, this could be important.

C. Weatherability: It has been predicted that colorants which would offer the best ultraviolet light protection for polyethylene would be those that absorb highly in the ultraviolet range and reflect the infra-red (5).

An ideal pigment in addition to having these characteristics would also have a very small particle size and be easily dispersed in the resin. Of all of the pigments available, carbon black comes the closest to meeting these requirements. Unfortunately it does absorb highly in the IR. In most applications this is no problem. However, in very fine filament or thin films the absorption of heat by 2.5% carbon black can lead to thermal degradation in a relatively short period of time. When properly compounded with a good thermal antioxidant this degradation does not occur.

Any pigment that will increase the opacity of the resin to UV light will offer some degree of protection. *Table 5* lists several pigments and their ability to protect linear polyethylene.

As one might expect, combinations of pigments modified by small amounts of carbon black results in colored resin

Table 3. Effect of Pigment Loading on the Electrical Properties of Linear Polyethylene

		1 Kc		1 Mc	
		K	DX	K	DX
Resin:	MARLEX 5000, Type 3				
	1% Titanium Dioxide (Rutile)	2.35	0.0002	2.35	<0.0003
	(Anatase)	2.35	<0.0002	2.35	<0.0003
	1% Mercadmium Red	2.35	<0.0002	2.35	<0.0003
	1% Cad.-Lithopone Yellow	2.35	<0.0002	2.35	<0.0003
	1% Cad.-Selenide Orange	2.35	<0.0002	2.35	<0.0003
	1% Phthalocyanine Blue	2.35	<0.0002	2.35	<0.0003
	1% Ultramarine Blue	2.35	<0.002	2.35	<0.0003
	1% Iron Oxide	2.35	<0.0002	2.35	<0.0003
	1% Phthalocyanine Green	2.35	<0.0002	2.35	<0.0003
	1% Channel Black	2.35	<0.0002	2.35	<0.0003
	2.5% Channel Black	2.64	0.002	2.62	0.004
	Control	2.35	<0.0002	2.35	<0.0003

Table 4. Effect of Pigment on the Weld Strength of Linear Polyethylene (Cylinder Temp., °F-475)

Run No.	Weld Strength (lbs. pull)	Tensile Strength (lbs. pull)
1 Control (No pigment)	89	100
2 Milled-Dry Blend	92	—
3 Dry Pigment Blend	88	—
4 Milled-Concentrate Blend	88	—
5 Concentrate-Dry Blend	18	—

with significant resistance to UV. *Table 6* shows Weatherometer data on small amounts of carbon black in combination with other pigments to give a grey, dark blue and dark green resin. Using a correlation of 400-600 Weatherometer hours/year of exposure in Oklahoma, a five year life could be expected. Caution should be used in predicting outdoor life from this type of data because of the role part geometry, use and geographical location play in the useful life.

It should also be noted that in compounding polyethylene for maximum outdoor life it is advantageous to use a UV stabilizer in conjunction with necessary pigments. Although these stabilizers, usually substituted benzophenones or salicylates, have limited compatability with polyethylene they may be added in sufficient concentration, either dry blended or compounded, to significantly increase the outdoor life of the resin. *Table 7* shows the affect of small amounts of UV stabilizer and pigment on the expected outdoor life.

Metallic or "Glitter" Effects

The use of powdered metals in polyethylene pigmentation systems is growing rapidly because of the attractive effects which may be produced. When the color of a competitive material, such as a painted metal part, is to be reproduced in polyethylene, the metallics are often required. However, special stability problems may be introduced by the codispersion of conventional pigments with fine metal powders. As the particle size of powdered metals decreases, the surface to volume ratio increases rapidly, affecting a corresponding increase in chemical reactivity. Therefore, in any such formulation, the colorants may be attacked by the fine metallics, resulting in a color shift. Here again the phthalocyanine pigments have proven particularly vulnerable to attack. For this reason, the thermal stability of each formulation containing a powdered metal component should be carefully checked. Normally high temperature injection molding or an oven residence test, as previously described are used.

When metallic blends are prepared in a Banbury mill, stability problems may be circumvented, or at least minimized, by the following technique:

(1). Blend all pigments except the metal in a normal milling run.

(2). Stop the mill and add the powdered metal to the banded resin.

(3). Mill for a few additional minutes and drop the batch.

This technique does not provide a high dispersion of the powdered metal, but will prove satisfactory for most applications. The same principle—*withholding the metal until the last phase of the processing run*—has also been successfully applied to extrusion and dry blending runs. Before using this technique, the compounder must verify the fact that the end fabrication operation will not approach the severity of conditions of the compounding step. Otherwise, the compound might prove unstable in the finishing operation.

Table 5. Effect of Pigment on UV Stabilization of Linear Polyethylene (Outdoor Exposure in Oklahoma)

	Control	6 Months	1 Year
	Tensile Strength, psi		
Titanium Dioxide (Rutile)	4440	3230	1120
Titanium Dioxide (Anatase)	4440	1770	480
Cadmium Yellow	4520	3860	3320
Cadmium Red	4410	4020	3050
Iron Oxide	4450	4560	4460
Phthalocyanine Blue	4360	2800	1320
Phthalocyanine Green	4610	4640	4610
Carbon Black, Monarch 74	4420	4580	4650

Table 6. The Weathering of Colored MARLEX Containing Small Concentrations of Carbon Black

Color	% Thermax	Control	Hours Exposed (Weatherometer) 3000 Hrs.	5000 Hrs.
Grey	1.2	4370	4280	4000
Blue	.3	4750	4600	3400
Green	.6	4650	4500	4200

Table 7. Life Expectancy of Linear Polyethylene to Outdoor Weathering

Formulation	Time (years)
Control (Unprotected)	¼-1
Resin + 1% Pigment	½-2
Resin + 0.5% UV Stabilizer	1½-4
Resin + 0.5 UV Stabilizer + 1% Pigment	1½-5
Resin + 0.5 UV Stabilizer + 1% Pigment*	4-6
Resin + 2½% Carbon Black (Small particle size channel black)	20

* Containing at least 0.30 carbon black.

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This article adapted from a paper presented at the 16th ANTEC—Chicago—January, 1960.

Ideas for Finishing Molded Plastics by . . .

Roll Leaf Stamping

Martin A. Olsen
OlsenMark Corp.

A useful technique in decorating by roll leaf is molding in clear plastic and decorating from the back (second surface). Parts such as automobile deck medallions, dashboard panels, horn buttons, etc. are made this way to prevent the finish from wearing.

DESIGN

Keep stamping area of the piece (top and bottom) clear of ribs, bosses or other projections.

Knockout pin marks, gate marks, and engraved information should be outside the marking or supporting area.

Keep marking and supporting areas as flat as possible. Curved areas can be hot-stamped with a curved die.

MOLDING

Adjust molding cycle to slow enough rate to allow proper cooling of molded piece.

Stamping die must match the surface of the molded item exactly.

Dies should be made of hardened steel.

Coloring raised letters, figures, panels, etc. can be done using silicone rubber dies. Roll leaf can be deposited on top of the raised areas in the molded article. The silicone rubber can be bought in sheet form vulcanized to a thin sheet of steel or aluminum. When using silicone rubber dies, mount the dies as close to the heat source as possible.

ROLL LEAF FORMULATIONS

Metallics–powdered bronze, gold and aluminum, vacuum plated pure gold and the new vacuum metallized imitation gold and silver. The new metallized products are primarily used to metallize confined areas in custom molded plastics.

Colors–soft matte finishes, hard lustrous enamels, and new transparent dye colors. Enamel finishes are solvent resistant.

—— ■ ——

Two November RETEC's to Feature Automation and Blow Molding

Two important dates on your technical meetings calendar are November 7 and 18 when the Ontario and Newark Sections will stage RETECs on "Automation" and "Blow Molding" respectively. Details of both follow briefly.

AUTOMATION IN INJECTION AND COMPRESSION MOLDING

Date: November 7, 1960

Place: King Edward Sheraton Hotel
Toronto, Ontario, Canada

Sponsor: SPE Ontario Section

Technical Program: Two concurrent sessions (both morning and afternoon) of five papers each covering new developments and trends in automation as applied to injection and compression molding.

Registration Fees:

Members	— Advance	$7.50
	On-Site	8.50
Non-Members	— Advance	9.00
	On-Site	10.00

Registration Chairman: John D. Glen
Canadian Industries, Ltd.
1303 Yonge Street
Toronto, Ontario

BLOW MOLDING COMES OF AGE

Date: November 18, 1960

Place: Essex House
Newark, New Jersey

Sponsor: SPE Newark Section

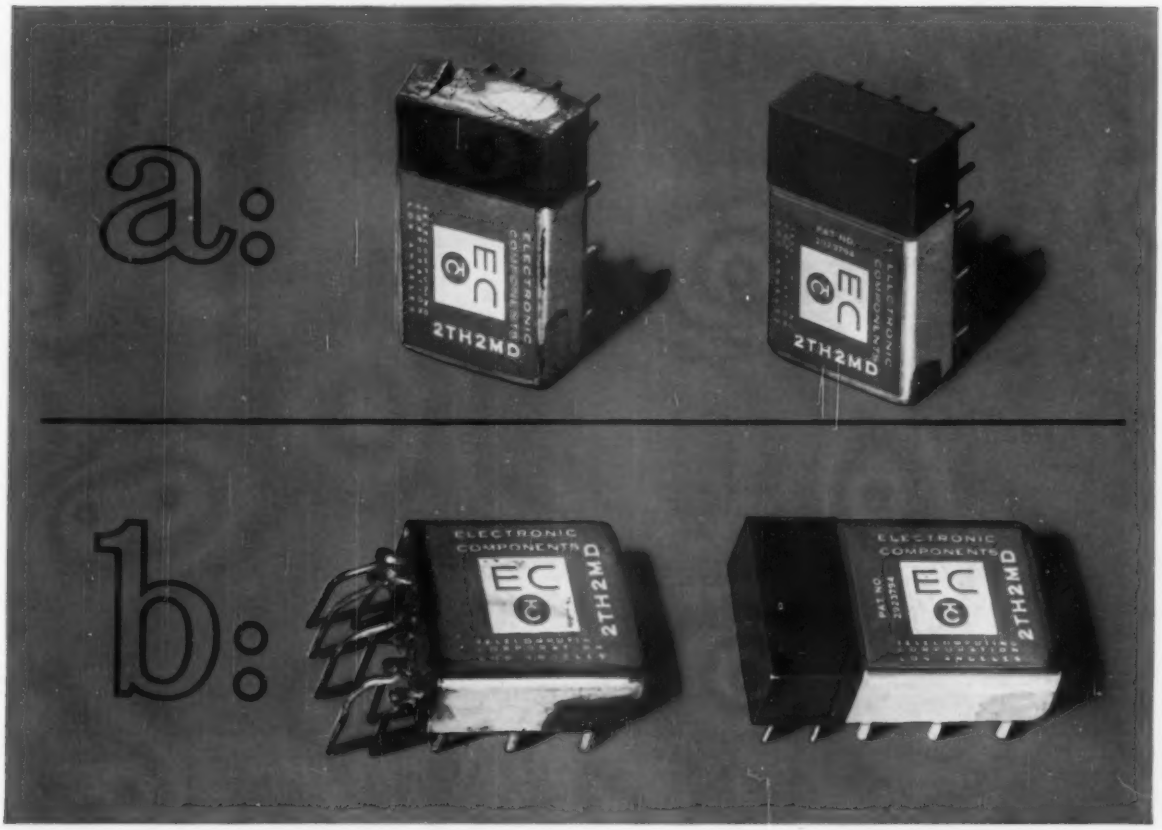
Technical Program: Comprehensive program encompassing all elements of this mushrooming segment of the plastics industry including history, applications and markets, forming techniques and equipment, materials, tooling and legal aspects.

Registration Fees:

Members	— Advance	$10.00
	On-Site	11.00
Non-Members	— Advance	13.00
	On-Site	14.00

Registration Chairman: David A. Jones
Celanese Corp. of America
290 Ferry Street
Newark, N. J.

DOW | THERMOSETTING RESINS



TESTS PROVE DOW EPOXY NOVOLAC

outperforms conventional epoxies under extreme stress!

Potting relay terminal connectors for the guidance system of one of America's new missiles, a major electronic component manufacturer made a series of torture tests . . .

TEST a: To determine the effects of prolonged heat on two terminal relay potting formulations—one a high quality conventional epoxy resin, the other, Dow Epoxy Novolac (D.E.N. 438). Both were placed in a 180°C. oven. After five hours, the conventional epoxy resin potting cracked. But after 100 hours of continuous 180°C. heat, the potted terminal made from Dow Epoxy Novolac was unharmed!

TEST b: To compare the ability of each potting to withstand the action of high-powered degreasing solvents. The ordinary epoxy resin formulation was completely dissolved after only 48 hours in the stripper. But the potting made from D.E.N. 438 showed no significant change, even after two weeks' immersion in the same solvent!

RESULTS: Proof once again that for potting, molding, encapsulating, laminating electronic components, or for any application where performance is critical, Dow Epoxy Novolac resins can provide the extra measure of physical and chemical stability necessary for success.

New applications for the Dow family of thermosetting polymers are being uncovered every day. If your application could benefit from their hardness, toughness, dimensional stability, and chemical resistance, call your nearest Dow sales office. Or write: THE DOW CHEMICAL COMPANY, Midland, Michigan, Plastics Merchandising Department 1966EX9.

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SOCIETY ACTION

SPE Public Relations ..... a Progress Report

Frederick C. Sutro, Jr.
Chairman,
SPE Public Relations Committee

Since last June when Council approved in principle implementation of the much-needed Society public relations program, SPE has made giant strides forward in this vital area. But, while these steps represent considerable improvement in our relations with others, we have come but a short distance along the road toward our goal. The possibilities and ramifications of our activities to establish SPE and its members with all of their publics are virtually limitless.

Our present program is geared to influence favorably toward the Society three major groups—industry, including the plastics industry and current and potential end-user industries; SPE members themselves; and prospective members. You will note that the general public is not one of the prime groups which we seek to influence in our favor. However, a planned program directed toward the three major groups cannot help but produce with the general public attendant side benefits for the Society and its members.

The program has and will be accomplished primarily by the written word-in releases, letters, reports and newsletters. It will be supplemented with other means of communications and contact and will, at one time or another, utilize every known media including radio, television and all segments of the press. While the Public Relations Committee is responsible for developing the policy and the program, implementation is a staff function for which Bob Forger at the Executive Office is responsible.

While it is recognized that personal contact is the most effective means of publicizing Society activities and accomplishments, the widespread contact required is impossible on a Society Officer or staff level. It is in this area, however, that the individual member can contribute substantially to the program. The collective efforts of members play a dominant role in creating a favorable opinion toward the Society and its members.

To maintain the steady progress necessary to achieve 1960 membership goals (right), the SPE Membership Committee urges that:

1. Sections step-up their membership drives when full-scale activities are resumed this month.
2. Every member who has not yet paid his annual dues, send them to the Executive Office as soon as possible.

Similarly, local Section public relations and publicity programs complement that of the Society. Opportunities on a Section level are more abundant than on a Society level because of the local flavor and personalities involved. For this reason and because local publicity more closely approximates personal contact, results can often be far more rewarding.

This area of local public relations has received the particular attention of the Public Relations Committee. One of its first projects will be appointment of Regional PR Advisors, all of whom are professional public relations executives from industry. Because of their knowledge, these advisors will be asked to serve as liaison between local media and Section Publicity Chairmen and the staff public relations director. Their services will involve advice on media, introductions and, in general, aid in establishing permanent public relations procedures in their area. Yet a second proposed project will be publication of a Section Publicity Handbook to guide Chairmen in their local public relations activities.

A major accomplishment during the summer was preparation and publication of the PAG brochure. Designed to explain more fully to SPE members benefits and opportunities for technical growth offered by PAGs and PACs, this brochure represents another step toward providing basic promotional literature on Society activities.

Yet another step in the same direction is a brochure entitled "Plastics as an Engineering Career" which will outline the vital role of the plastics engineer and scientist in industry. Now in preparation for the Education and Membership Committees, it will simultaneously promote to prospective high school and college students the plastics industry, science and engineering, and SPE Student membership.

While implementing the above projects, the Committee has been particularly attentive in maintaining and, in most cases, increasing the tempo of existing public relations activities. For instance, participation of Society Officers in local Section meetings and RETECs has been widely publicized and advance details of RETECs have been disseminated more broadly and with increased frequency than ever before.

This fall results of Society elections will be widely released and an integrated promotional program for ANTEC kicked off. Personal contact with the editorial staffs of leading trade and business papers has already been stepped up.

Last and least glamorous public relations activity—but often the most rewarding—is what might be termed the "information service". A vital part of the program, this service provides answers to specific requests for information, many of which have the potential of generating an outstanding story, one that is seldom possible from a "canned" release.

As previously mentioned, we have all but limitless opportunities before us to put the Society, and its members in their rightful place in the minds of the industrial, engineering and scientific publics. We intend to take advantage of each opportunity at the earliest possible moment in our program to establish SPE as a Symbol of Professional Eminence and to develop and increase the professional stature of SPE members.

—— ■ ——

edited by
Thomas A. Bissell,
SPE Executive Secretary

SPE Publications for Sale

★ **16th ANTEC Preprint Book**—Volume VI, 1960, Chicago, 83 papers. $7.50 members; $12.50 Non-members. Single preprints of individual papers, Vol. VI, while they last, $0.25 each, members; $0.40 each, non-members.

★ **1960 RETEC Preprint Books—Plastics in the Petroleum and Chemical Industries**—North Texas Section, 8 papers, 63 pages. $2.50 members, $3.75 non-members. (see program, p. 260, March 1960 SPE Journal).

Just Published: **New Horizons in Vinyls, and Plastics in the Shoe Industry**—Eastern New England Section, 13 papers, $3.00 members; $4.50 non-members. (See program, July, 1960, SPE Journal, p. 743.)

Also available

★ **NATEC Preprint Book**—Volume I, 1959, Los Angeles, 20 papers. $5.00 members; $7.50 non-members (See program, September SPE Journal, page 788, and Abstracts on pages 815-817).

★ **Stability of Plastics**—Baltimore-Washington Section; Nine 1000-word abstracts. $1.00 members; $1.50 non-members (See program page 897, Oct. SPE Journal).

★ **Plastics in the Shoe Industry**—St. Louis Section, 11 papers, $3.00 members, $4.50 non-members. (See program, September SPE Journal, page 820).

★ **Plastics in Packaging**—Golden Gate Section, 12 papers, $3.00 members; $4.50 non-members. (See program, October SPE Journal, page 899).

OTHER 1959 RETEC PREPRINT BOOKS

★ **Vinyl Plastics**—Cleveland Section, 8 papers. $2.50 members; $3.75, non-members. (See program, SPE Journal, August, 1959 issue, p. 745).

★ **Plastics Finishing**—Buffalo Section, 4 papers, $2.00, members; $3.00 non-members. (See program, SPE Journal, September, 1959 issue, page 823).

★ **Encapsulation, Printed Circuits, and Fluidized Bed Processes**—Northern Indiana Section, 15 of 23 papers presented. $3.00, members; $4.50, non-members. (See program SPE Journal, April, 1959, p. 319).

★ **Plastics in the Automotive Industry**—Detroit Section, 4 papers, $2.00, members; $3.50 non-members. (See program SPE Journal, May, 1959, p. 443).

★ **A Designer's Look at Reinforced Plastics** from the Pleasure Boat; Aircraft and Missile Industries Viewpoint—North Texas Section, 6 papers. $2.00, members; $3.00, non-members. (See program SPE Journal, April, 1959, p. 324).

SPE PLASTICS ENGINEERING SERIES

Vol. II—"Processing of Thermoplastic Materials", E. C. Bernhardt, Ed., Reinhold Publishing Company 1959, 705 pages. $14.40, members; $18.00, non-members.

SPECIAL PUBLICATION

★ **Plastics for Architects, Artists and Interior Designers**, by Armand G. Winfield. An illustrated survey of some of the best uses of plastics in the building and decorative fields. $2.25

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Professional Finishing Techniques Promoted Through PAG-PAC Program

Thomas Hayden, *Chairman, Finishing PAG*
(Bee Chemical Co.)

PAG Progress

Finishing PAG

A recent experiment in the Chicago Section, jointly sponsored by PAG-PAC, drew an audience from four states for an evening program entitled "Finishing Foremen's Forum". The forum, held concurrently with the regular after-dinner program of the monthly Chicago SPE Meeting, attracted a total of 65 people. Three speakers, each qualified to speak on various phases of "First and Second Surface Decorating of Indented Letters" and each limited to ten minutes commentary, covered the subject briefly and then opened the session to audience participation. Armed with molded, decorated parts for demonstration, the audience enthusiastically carried the remainder of the program.

This session, and the response engendered in the audience, served to point up the need for future technical programs that could deal with various phases of Finishing techniques. It indicated that many other Sections can benefit from such programs, particularly those situated near heavy industrial areas throughout the country where Finishing is a subject of paramount interest.

These workshops, based upon the idea of combining qualified speakers with a highly interested participating audience are also the key to added membership for the Society. Such PAGs can do more than any other single activity to prove to potential members the Society is an organization that performs valuable advisory service to other industries as well as to the plastics industry.

As witnessed in the Chicago session, the need for dissemination of information on professional finishing techniques exists in no small degree. This was clearly demonstrated several times through the eagerness of certain participants to "stray" from the main topic to questions on finishing problems they were currently experiencing (serving to give the panel possible topics for future sessions).

It is worth noting that a good percentage of those present were not SPE members. The appeal of the program was simple, the approach specific. Any PAG organized along the line of providing concrete, immediate knowledge to an individual to aid in his personal professional advancement is bound to succeed. This was exactly the reaction to the Chicago experiment. Many who attended the session felt they walked away with answers to problems that could be immediately put to work on their job. It would seem obvious then it is quite desirable to continue such sessions on a periodic basis and to maintain the level of interest with qualified speakers. The outcome will be new members for Finishing PAC and potentially loyal participants in PAG.

The month by month activity of PAC is imperative to strong membership interest and results in a stronger Society and unquestionable increase in individual growth.

The Finishing PAG Executive Committee is planning a series of Workshops to be held at various Sections throughout the country to duplicate the success of the Chicago experiment and to herald the formation of more PAC-Finishing Groups.

Realizing the value of PAG is measured only by its accomplishments and not merely by proving its existence, other activities are being conducted, notably participation in ANTEC. Earlier this year the 1961 ANTEC Committee asked the Finishing PAG Executive Committee to assist in stimulating a Finishing Session for the 17th ANTEC to be held in Washington, D. C. in January by encouraging potential authors. The Executive Committee responded by making a careful analysis of subjects which would constitute a strong session for the ANTEC. Recognized experts in various phases of the Finishing industry were contacted and asked to submit abstracts based on these topics. The Committee has succeeded in developing and recommending to the ANTEC Committee what it believes to be a very complete and specific program designed to attract finishing people at different job levels from all sections of the country. (It is worth mentioning that the Committee was successful in obtaining three of the seven papers from processing plants; no easy task as those of you who have served on Speaker's Committees will appreciate).

The program that has been recommended, but as yet not finally approved by the ANTEC Committee at this writing, consists of the following seven papers:

1. Design for Plastic Finishing
2. Methods to Eliminate Mechanical Finishing of Thermoplastics
3. Automatic Spray Painting
4. Hot Stamping of High Luster Metallic Colors
5. An Analysis of the Relationship of Design to Performance of Vacuum Metallizing Machines
6. Automation in a Finishing Department
7. Effect of Coating Properties Upon Operational Sequence of Multi-Method Finishing

The program is broad enough to attract people doing various types of finishing, but yet individually the papers are specifically designed to impart concrete and fresh information. This program is bound to arouse a good deal of interest on the part of finishing people who are not aware the SPE is gearing to provide a service much in demand. Your attendance at the 17th ANTEC and your participation in the PAG business meeting can do much toward helping to promote these activities to non-members and help further the cause of the Society.

—— ■ ——

edited by
Frank W. Reynolds, *PAG Administrator*
(International Business Machines, Inc.)

Grueling
use-test pits
monomeric
vs. polymeric
plasticizers

Some years ago a vinyl upholstery manufacturer decided to field-test new materials for truck and transportation upholstery using a wide variety of monomeric and polymeric plasticizers, including Plastolein 9720. To compare *permanence* and *durability*, the different materials were installed on city bus drivers' seats. Here, seat upholstering would certainly be exposed to extraordinary abuse almost around the clock . . . continuous rubbing and flexing, city grime and grit, oil and grease.

After a certain period of time, all the upholstery containing monomeric plasticizers had failed. But all those made with polymerics, including Plastolein 9720, were still in excellent shape. With this evidence, the manufacturer concluded that only a polymeric plasticizer would meet its standards for truck and transportation upholstering, and protect its reputation. And Plastolein 9720 was chosen on the basis that it was the *lowest cost of all the fine polymerics tested.*

Today, Plastolein 9720 is *still* the lowest cost ploymeric plasticizer, and is *still* being used by this and many other manufacturers in such heavy-duty goods. Why not check 9720 yourself? Write Dept. J-9 for literature and sample.

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Emery Industries (Canada), London, Ontario—Export Department, Cincinnati

NEW BOOKS

PROPERTIES AND STRUCTURE OF POLYMERS

Arthur V. Tobolsky (John Wiley & Sons, Inc., 321 pp. $14.50)

This book outlines some of the basic principles of the mechanical behavior of polymers and attempts to relate that behavior to molecular parameters. This work does not attempt to cover the whole field nor teach elementary theory. Rather, it develops the mathematical structure in a given topic only as required for the generalization of experimental observations.

Prof. Tobolsky, being one of the earliest and original workers in the field, is eminently qualified to write on these topics.

The section on "The Five Regions of Viscoelastic Behavior" is particularly well done with a thought-provoking discussion of plastic applications in terms of corresponding viscoelastic states. The argument here is that variations of chemical constitution, while important for specific solvent resistances, etc., are necessarily limited in scope because of the requirements for certain transition ranges and viscoelastic responses imposed by a particular application.

This book is recommended to the serious student of the behavior of polymers, as being a clear and authoritative exposition of selected basic topics.

Dr. E. H. Merz
Continental Can Co.

CLASSIFICATIONS OF HIGH POLYMERS: A REVIEW

Prepared for IUPAC by R. Houwink with collaboration of H. Bouman (Butterworth & Co. (Canada) Ltd., 54 pp., $2.25)

The increasing scope, complexity, and use of plastics and high polymers makes the problem of classification increasingly important to everyone concerned with this field. The International Union of Pure and Applied Chemistry has been actively working on this problem since 1953, and the "present report is a critical and objective review of all of the systems, both published and unpublished", which have been proposed for consideration. 27 classification systems are described briefly and some critical comparisons are made.

A reading of this report indicates that it will be difficult, if not impossible, to devise a single system of classification which will meet the needs of all persons interested, including librarians, scientists, patent documentalists, manufacturers, and consumers. The ideal classification system would (1) include all forms of high polymers, such as plastics, elastomers, and fibers, (2) accurately describe the composition and structure of the polymer, (3) give detailed information as to the properties of the material, (4) be equally useful for all languages, and (5) not be too complicated for general use.

Although no one of the systems proposed has all of these desirable characteristics, it may be possible to provide two or more systems which will be useful for specific purposes. For example, the Universal Decimal Classification (UDC) is most useful for librarians, while the German system, or a combination of the British, Swiss, and Hoekstra systems, might be more useful to many users of molding materials.

This booklet does not attempt to give the final answer to this problem, but gives an excellent picture of its complexity and the work done to date. It should be a convenient source book for anyone interested in this subject.

Benjamin M. Walker
Resistoflex Corp.

AMINO RESINS

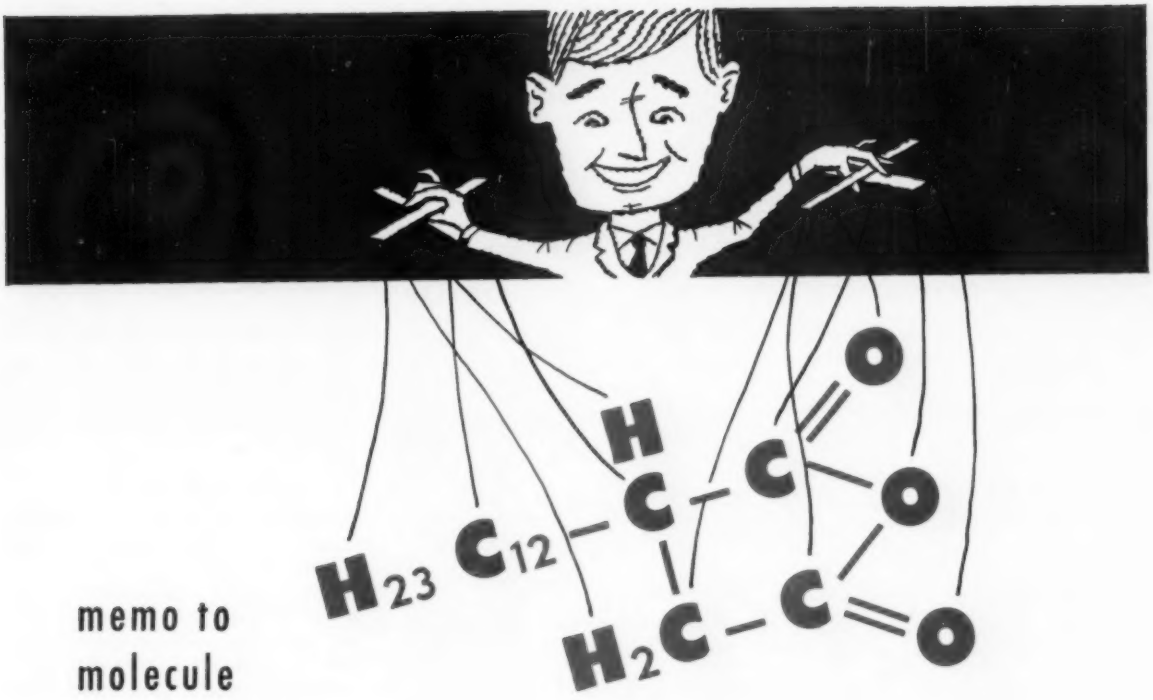
John F. Blais (Reinhold Publishing Corp., N. Y., 220 pp. $4.95)

The author's intent in this, the thirteenth volume in the Reinhold Plastics Applications Series, is to describe the commercially important applications of amino resins and to relate the various available resins to these applications. The first three chapters of this book cover the history, chemistry, and manufacture of amino resins. The materials discussed include urea and melamine resins and their variations, as well as the less common ethylene urea and benzoguanamine resins. The remaining seven chapters deal with the applications of these resins in compression molding, adhesives, laminations, textiles, paper treatment, surface coatings, and miscellaneous products. These chapters include descriptions of the equipment used, typical resin formulations, and discussions of the important physical and chemical variables by which product properties are controlled. An adequate index is provided, and sixty-eight references to the literature are given.

The information is presented in semi-technical language so that it can be understood by anyone with even a slight knowledge of plastics. A large amount of data from resin producers and other sources is shown in tables throughout the text and many illustrations are included. The application chapters are comprehensive enough to give a good idea of what would be necessary for the successful use of amino resins. Although the chemistry chapter is not as complete as the others, it has the most references.

This writer believes that the author has succeeded in his purpose very well, and this book is recommended for anyone interested in acquiring a knowledge of amino resin applications.

Richard H. Martin, Jr.
Monsanto Chemical Co.



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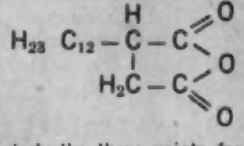

Note particularly the three points for addition reactions as steps toward new end products. Note also the positions of the oil-soluble alkenyl group and the hydrophilic reactive anhydride end.

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WRITE FOR TECHNICAL BULLETIN I-8

This six-page technical bulletin gives chemical and physical properties, principal reactions, infra-red absorption spectrogram, viscosity curve, suggested uses and a bibliography. A copy of this bulletin and a liberal working sample will be sent on request. Our Development Chemists will be glad to provide additional assistance to those whose work may lead to volume use of National Dodecenylsuccinic Anhydride.

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PLASTICS AROUND THE WORLD

This month's column has been made possible through the contributions of these abstracters:

Joseph B. Wolheim (Tworzywa-Guma- Lakiery)
Malcolm G. Bourne, Jr., (Revista de Plasticos)
John J. Shay (Electrical Manufacturing)
Leonard S. Buchoff (Materials in Design Engineering—March, April, May)
James P. Harrington (Materials in Design Engineering—June, and Rubber Age)
Dr. Albert Lightbody (Australian Plastics and Rubber Journal)
Dr. Hans Mayer (Industrie Des Plastiques Modernes)
Walter A. Gammel, Sr. (Rubber and Plastics Age)
James M. Margolis (Der Plastverarbeiter and Kunststoff Rundschau)
Charles S. Imig (Kunststoffe)

Poland

TWORZYWA-GUMA LAKIERY

JANUARY-FEBRUARY 1960

Melamine Decorative Laminates—(authors—J. Brzezinski and Z. Wirpsza)

The author discusses the raw materials used in melamine decorative laminates, the paper and the resin. The article publishes drawings of the equipment used in impregnating, drying, and curing the laminates. ASTM standards (U.S.A.) for decorative laminates are also given.

Trends in the Development of Urea Based Adhesives—(author—Stanislaw Maciaszek)

The author discusses the use of urea-formaldehyde resin in adhesives. These adhesives, according to Mr. Maciaszek, have the following shortcomings:

1. They contain free formaldehyde which irritates the skin and has an obnoxious smell.
2. They craze when used as thick glue lines in assembly gluing.
3. They are not resistant to boiling water.
4. They have a limited pot life.

The article then describes modifications to the resin in order to overcome these difficulties. This can be accomplished by incorporating into the adhesive urea, which will reduce the free formaldehyde, and resorcinol, which will improve hot water resistance of the adhesive.

Mr. Maciaszek discusses other additives in order to render the adhesive craze resistant and to prolong its pot life.

Spain

REVISTA DE PLASTICOS

MARCH-APRIL 1960

Influence of Molecular Distribution on the Viscosity of Plastisols—pp 79-86

Molecular fractions of polyvinylchloride resins are compared by differences in their respective solution viscosities. This technique is regarded as a measure of molecular weight of the various PVC resins as well as method of determining molecular weight distribution.

To be applicable to plastisols, the author concludes that a PVC resin must have a high specific viscosity and an absence of short polymer chains. Both of these factors determine the viscosity stability of plastisols. Many charts and graphs give the article good experimental support.

United States

ELECTRICAL MANUFACTURING

MAY 1960

Plastics Molding Materials for Structural and Mechanical Applications—(authors—H. E. Barkan and A. E. Javitz)

A review of plastics molding materials, based on structural and mechanical properties and design parameters. Newer materials are described in detail. Significance of test methods is discussed. Supporting tables and graphs. First in a projected series of articles on functional plastics for the design engineer.

JUNE 1960

Cast-Resin Applications in Switchgear and Transformers—(author—Wilhelm J. K. Oburger)

In contrast to practice in the United States, where cast resins are primarily used for embedment and encapsulation of electronic components and circuit assemblies, European engineers have made wide use of these resins (particularly epoxies) in switchgear and transformers. This article describes application techniques and illustrates typical designs.

JULY 1960

Epoxy Resin System in High Reliability Transformers—pp. 132-135

A report on epoxy systems to meet severe thermal vibration, moisture and electrical performance qualifications for transformers. Test data for evaluation of materials under these conditions are presented. Materials and design parameters of resins-components systems are explained for optimum performance.

MATERIALS IN DESIGN ENGINEERING

FEBRUARY 1960

What's New in Fluorosilicone Rubbers

Recent Developments in these fluid resistant rubbers include improved processing compounds, availability of a master batch, cost reduction possible by blending with less expensive rubbers, and room temperature vulcanizing materials. Charts and graphs describing the various fluorosilicones are included.

MARCH 1960

Low Cost Coatings for Metal Products—pp. 124-133

In this comprehensive article there is a section dealing with cellulosic, alkyd, oleoresinous varnish and bituminous coatings.

Molded Vinyl Plastisols—pp. 110-113

The versatility of flexible PVC is the key attribute of vinyl plastisols.

In-place molding provides permanently attached seals and gaskets. Rotational casting produced totally enclosed hollow parts at high production rates. Slush molding provides economical small and large production of hollow shapes, open at one end. Dip molding onto mandrels, solid casting and coatings are also described.

APRIL 1960

New Epoxies—(Authors—S. Miller and V. Chase)

Two articles describe epoxies produced by epoxidizing unsaturated compounds. The first gives a rundown of an impregnating resin that yields laminates of superior high temperature properties. The other concerns a series of epoxidized polyolefins that react readily with peroxides and acid anhydrides to yield light, heat resistant castings and laminates.

Organic Semiconductors—(Author—W. Brenner)

Organic semiconductors can be made and modified by irradiating and pyrolizing or impregnating with metals polymers such as polyacrylonitrile and ion-exchange resins. These materials have high Seebeck coefficients and are stable at elevated temperatures.

The phthalocyanines are also under study.

MAY 1960

New Flourocarbon Plastics Will Mold Readily—(Author—M. W. Riley)

Polyvinylidene fluoride, Pennsalt's RC-2525, offers excellent resistance to weathering, chemical and heat. Temperature range −80°F. to 300°F. Electrical properties are not outstanding.

Potting and Encapsulation Materials—pp. 123-127

A general description and table of properties are given for hot melts, styrene polyesters, epoxies, silicones, liquid elastomers and foams.

Tensile and Impact Strength of Ten Epoxy Adhesive Formulations—pp. 136-138

Data is presented at −65°, 73.5° and 160°F. for steel to steel joints.

Awards for Material Selections—pp. 139-162

Plastics played a big part in the competition. Wide use of plastics was made in the lubricating system that took first prize. Silicone rubber was used in force ring, urethane in pinch roll coating, vinyl in paper making machinery, epoxy-glass encapsulation in fan assembly.

JUNE 1960

Appliances: What Materials Are Next—pp. 121-130

A thorough survey of the many materials used in the manufacture of the major household appliances. Many recent investigations of plastics are considered and the author estimates the possible success in overcoming the technical and economic problems, which are described in some detail, before the plastics will replace metals or other plastic materials. Structural materials, decorative trim and

for your finishing operations

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accomplish the *QUICK* Color Marking and Decorating Operations on your molded and fabricated plastic parts and products.

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"PLASTIC MARKING PIONEERS"

"The Original Marking Specialists"

IF YOU HAVE A STAKE IN PRODUCING FOOD WRAPS

HERE IS THE MOST EFFICIENT, NON-TOXIC PLASTICIZER MADE

Harchem Dibutyl Sebacate has been FDA approved as a non-toxic plasticizer for food wraps. Equally important, it has been user-approved for the following reasons:

Compared with other plasticizers for food wraps, Dibutyl Sebacate offers . . .

Best Low Temperature Properties . . . Best Heat Stability in Terms of Discoloration and Odor . . . Lowest Degree of Tack . . . Low Initial Viscosity for Plastisols . . . Contributes to Thixotropic Properties

	DIBUTYL SEBACATE	NON-TOXIC PLASTICIZER X	NON-TOXIC PLASTICIZER Y	NON-TOXIC PLASTICIZER Z
Efficiency Level to obtain equal moduli (parts per hundred)	39	52	54	53
Low Temperature Flexibility Tf °C @ 135,000 psi	-36.6	-22.8	-24.8	-15.7

Whether judged on a basis of performance or cost, you'll find Harchem **Non-Toxic Dibutyl Sebacate** a superior plasticizer for food wraps.

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hardware, coatings, finishes, and thermal insulation materials are among the items discussed.

High Temperature Plastics: Where Do We Stand—pp. 132-134

A concise report on recent developments in the search for polymers which would be suitable for service at temperatures above 500°F. Some present polymers are suitable for short times at very high temperatures, e.g. as found with nose cones of missiles. Commercially available polymers are only suitable up to 500-600°F. for long time (>200 hours) operation, with possible intermittent use up to 600-800°F. A few laboratory prepared polymers now give some hope of approaching 750°F. for long time operation.

RUBBER AGE

MAY 1960

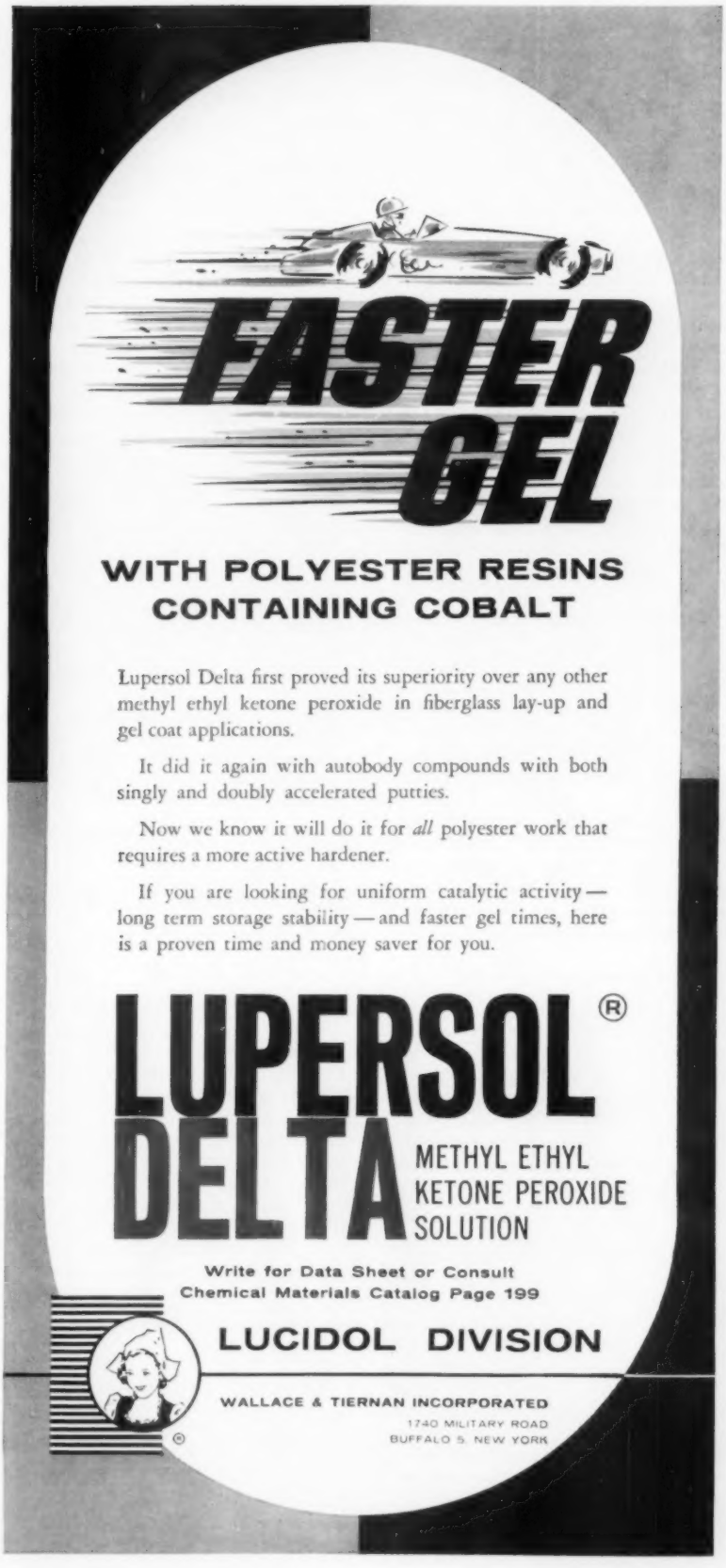
Characterization of PVC Resins by the Conductivity of Solvent Extract—pp. 279-285

Interlaboratory tests showed that the resistivity of PVC compounds decreased sharply when resins with high extract conductivity were used. A rapid test, which can be performed with usual laboratory apparatus, has been developed to remove extractibles from PVC resins and then determine the electrolytic conductivity of the extract. This work was done in conjunction with ASTM D-20 and reported at the 1960 ANTEC.

JUNE 1960

Elastomeric Properties of Ethylene-Propylene Copolymers—pp. 459-467

A detailed discussion of the development of an elastomer film from copolymers of ethylene and propylene. Mechanical mixtures of the two polymers are not elastomeric; but the copolymer with 72.5% ethylene has a rebound vs. temperature curve which more closely approximates that of natural rubber than do any of the usual synthetic rubbers. A decrease of the ethylene content of the copolymer to 52% results in a curve similar to styrene butadiene rubber, while at 30% the copolymer is approaching the curve found with du Pont's "Hypalon" chlorosulfonated rubber. Cross-linked copolymers closely follow the predictions of the statistical theory of rubber elasticity.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Australia

AUSTRALIAN PLASTICS AND RUBBER JOURNAL

MARCH 1960

Medium-Density Polyethylene in Coatings—pp. 32-35

A large amount of data has been presented which can be of considerable importance to the polyethylene coater or the user of polyethylene-coated materials. The significant points to consider in reviewing this material are these:

First, where greaseproofness is required, the use of intermediate-density polyethylenes can offer properties comparable to low-density polyethylenes at lower coating weights or in some instances offer properties not reasonably attainable with low-density polyethylenes.

Second, where Water Vapor Transmission Rate is of importance, coating weights may be substantially reduced over low-density polyethylenes, thereby reducing cost in spite of the higher prices of the intermediate-density resins.

Third, where abrasion resistance is important, intermediate-density polyethylenes offer advantages not available with those of low density.

Finally, all these properties are attainable using presently available equipment without having to sacrifice extrusion behavior.

APRIL 1960

"Korlite" Panel Cored with Rigid Urethane—pp. 19-21

Multi-story buildings in several Australian cities are being clad with a new type of building panel. The giant Chevron Building in Sydney, office blocks, hotels, and military barracks are some of the projects completed or in hand.

These panels are of sandwich type, the outer skins of any material specified by the architect while the core is rigid urethane foam, either alone or reinforced with tubular or corrugated materials. The twelve-story office block in Melbourne is faced with panels of blue porcelain enamelled steel, each panel completely sealed, filled with rigid polyurethane and reinforced with tubes. These panels are only one to two inches thick yet have been approved by building and fire authorities.

France

INDUSTRIE DES PLASTIQUES MODERNES

MAY 1960

Improvements in the Field of Pipe Extrusions — (Authors — Dominghaus and Schiedrum)

While extrusion techniques have reached a satisfactory level, further improvements in the quality of the endproduct and in the quantity of output can be achieved. The authors discuss these possibilities for the field of low pressure polyethylene pipe extrusion by comparing the advantages and disadvantages of the use of single or double screw extruders in combination with axial, cross or offset heads. The technique of biaxial stretching is also described and evaluated.

Plastic Foams—(Author—Y. Salmona)

A comparison is made of production techniques and applications of polyurethane (flexible) and cellular polystyrene (rigid) foams. The technical data, covering mechanical and chemical properties, are set up and a testing instrument, especially devised for testing the rebound of the endproducts, is described.

England

RUBBER AND PLASTICS AGE

JUNE 1960

New Thermoplastic Copolymers (Italy)—p. 643

From binary copolymer of dimethyl itaconate and styrene the proprietary "Dialux A" was derived. "Dialux B", a ternary copolymer of methyl itaconate styrene, and acrylonitrile, has much better resistance to automotive fuels, and improved mechanical properties. Hardness of "A" and "B" higher than molding polystyrene. Shock resistance comparable to polymethymethacrylates.

Hong Kong's Plastic Flowers Industry—p. 640

There are 400 factories making plastic flowers in Hong Kong. Some 68% of flowers shipped to U.S. and 14.5 to England.

Over 1600 7½ oz. and 75 2 and 3 oz. injection molding presses were purchased in 1959 to bring totals to 2,800 and 120, respectively.

Newest designs use PVC for petals to improve life-like texture; polyethylene is used elsewhere in 65 plants.

(The editor cautions: "We would certainly issue a word of warning to other molders not to enter too enthusiastically into this field. The market is already well catered for, and competition will undoubtedly be fierce.)

Plastics in the Far East—p. 639 and p. 652

Assuming "Far East" to be area east and south of Siam a wide divergence in progress in plastics is noted.

Japan, for example has quadrupled since four years ago production of polyvinyl chloride, caprolactam, and polyvinyl alcohol; They have tripled production of urea formaldehyde, vinyl acetate, and polythene.

Principal exports are toys and buttons. The volume of buttons has increased from 399,000 £ to 1,091,000 £. PVC is also exported in volume.

Notable development has been PVA for "Vinylon", a textile fiber developed in Japan.

Since separation from Singapore, Federation of Malaya market has become one of the most promising markets. High price of rubber has helped their economy. Butadiene—styrene copolymers used in manufacture of microcellular soles for sandals.

Germany

DER PLASTVERARBEITER

FEBRUARY 1960

"Derex" Twin Screw Extruder—p. 100

The Dusseldorf Iron Works which manufactures granulators, film and foil equipment and other machinery is producing two types of twin screw presses with 92 mm. and 60 mm. extruders. These extruders were developed in close collaboration with the plastics industry and distinguish themselves with their safety elements and hourly output.

Under optimum conditions and considering a favorable exhaust aperture and normal material, the 92 mm. extruder can process 140 kilograms per hour polyethylene and polystyrene, 120 kilograms per hour rigid PVC and 200 kilograms per hour flexible PVC. The figures for the 60 mm. extruder are approximately half the above numbers.

Continued on page 1073

U.S.I. POLYETHYLENE NEWS

A series of advertisements for plastics and packaging executives by the makers of PETROTHENE® polyethylene resins

Packaging Notes

Low-cost contour packaging equipment (below) tight-wraps any shape product with a special formula transparent polyethylene film. Machine's key feature is a heated-air shrink tunnel. No liquid dip is required; there is no appreciable change in product temperature. According to the manufacturer, low cost of equipment and polyethylene film plus reduced handling and labor expenses make this machine ideal for packaging almost any item, even at relatively low production rates.

A one-piece brush and cap for containers of paste, shoe polish, rubber cement and the like employs a polyethylene shank and flange, preassembled to a metal cap, to prevent seepage and evaporation of liquid contents. The molding has a retaining bead which holds the flange firmly against the metal, eliminating the need for riveting or soldering and a washer. Swab is stapled in place. Designed to replace a steel shank and cap, the assembly comes in a range of sizes and colors with application swabs to fit any production equipment.

"Plastics Packaging—Problems, Potentials, Profits" is the theme of a Packaging Institute seminar to be held September 28th at the Statler-Hilton Hotel, New York City. Twenty panelists, including a representative from U.S.I., will participate in the discussion, which will cover all phases of packaging—from resins to end use. For details, write to Packaging Institute, 342 Madison Ave., New York 17, N. Y.

U.S.I. Introduces Two New PETROTHENE Polyethylene Blending Resins

Also Useful for Injection Molding into Items with High Flexibility

U.S.I has developed two new high-melt index PETROTHENE resins ideal for blending with lower flow polyethylene resins for non-critical injection molding applications. The high flow characteristics of these resins can serve to greatly increase the flow of other available resins to meet product and production requirements. These resins are also usable without blending for injection molding of non-critical items where an extremely high degree of flexibility is required.

Artificial flowers such as these can be injection-molded from U.S.I. PETROTHENE 270 polyethylene resin.

PETROTHENE 270 has a melt index of 70 and a density of .912. It is an ideal resin for molding soft items such as artificial flowers. Key properties include *very* high flow rates, *very* high flexibility and excellent low-temperature impact strength in molded items. Because this high flow resin can be molded at an extremely low level of locked-in stresses, it shows excellent low-temperature impact strength according to practical type tests on molded items conducted at U.S.I.'s Polymer Service Laboratories.

In addition to high flexibility and resistance to cracking at low temperatures, products molded from PETROTHENE 116 have high gloss and excellent appearance. This resin can be used to form large non-critical molded items—not as flexible as those made from PETROTHENE 270, but still very flexible. Its density is 0.919, melt index 33.0.

Blending Data Available

U.S.I. has prepared graphs for determining the weight percent of PETROTHENE 270 or PETROTHENE 116 required with any lower-melt index resin to obtain a blend of any desired intermediate melt index.

To obtain these graphs or additional technical data, write Technical Literature Dept., U.S.I., 99 Park Ave., New York 16, N. Y.

Process Improves Bonding Of Polyethylene To Metal

A new process for bonding polyethylene to metal produces unusually strong bonds, limited only by the strength of the plastic itself. The process is ideally suited to copper alloys containing over 85% copper, but the inventors feel it will work with any metal that can be copper plated.

In this process, polyethylene is molded directly to oxide-coated metal. Key to its effectiveness is chemically treating the metal to form a cupric oxide film since neither a cuprous oxide film nor a thermally oxidized surface will form strong bonds. Bond strengths, measured with the conventional Instron machine, are 20 to 40 lbs. per inch of width, in contrast to the best previously attainable strengths of 5 to 10 lbs.

According to the developers, the process will make possible pressure-tight seals between polyethylene and copper in repeater units of submarine cables —long a problem. Out of it, too, may come advances in flexible printed circuits, microwave devices and other electronic equipment where the excellent electrical properties of polyethylene can be utilized. And it may spur wider use of metal-polyethylene panels as structural materials in the construction field.

How to Improve Heat Sealing

A new U.S.I. technical data sheet shows how to solve major problems encountered in heat sealing polyethylene film. Such difficulties as non-uniform seals, weak seals, and film adhesion to the sealing jaw are discussed. For copies of the data sheet, "Improve Heat Sealing by Modifying Equipment," write U.S.I's Technical Literature Dept.

Polyethylene Plus Aggregate Forms New Paving Material

A new paving material compounded of pigmented polyethylene and aggregate promises to bring color-coding of roads and runways closer to reality. It can be mixed and applied (in a one-inch layer) using conventional machinery and methods. Brilliant white test curbing being installed above defines road boundaries. Other possible uses: multi-colored home driveways, tennis courts, sidewalks, swimming pools.

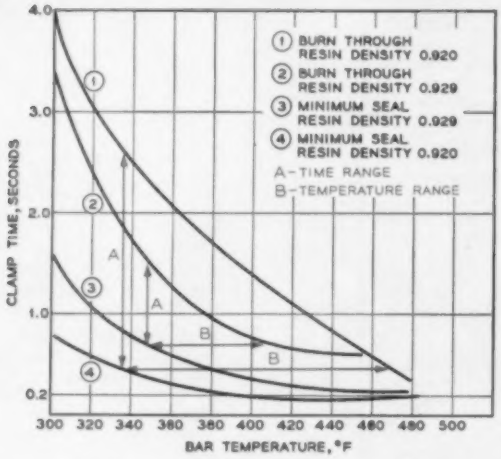
U.S.I.
Series V, No. 5

POLYETHYLENE PROCESSING TIPS

MACHINE CHARACTERISTICS AFFECTING HEAT SEALS

Polyethylene film heat seals easily to form air-tight, moisture-proof containers for a wide variety of packaging applications. However, sealing equipment that is poorly designed or improperly used may cause such problems as non-uniform seals, weak seals, or film sticking to sealing jaws.

Many sealers that were adequate when only low-density polyethylene resins were available do not provide the control needed for higher-density, high-clarity films now on the market. The reason, shown graphically below, is that as resin density increases, temperature range between minimum seal and burn-through of film narrows. This range may be narrowed still further by gussets in bags or variations in film gauge.



Increasing density from 0.920 (PETROTHENE® 210) to 0.929 (PETROTHENE 239) results in a narrowing of the heat-seal range between minimum seal and burn-through. (0.5 mil blown tubing)

Temperature Variations

A common cause of poor heat seals is excessive temperature variation along the length of the sealer blade. Best results are obtained when the temperature varies less than 15 degrees F.

With jaw-type sealers, such control may be achieved by replacing or repositioning the heater elements, or if necessary, by replacing the entire sealing jaw. Similar measures work for band-type sealers as well.

It is difficult to measure temperature differences on impulse sealers, but easy to insure desired temperature uniformity. These sealers function by passing an electric current through a wire while it is in contact with the film to be sealed. Temperature differences arise from variations in the diameter of the wire, which offer varying electrical resistances. Hence, regular visual inspections are recommended. When nicks or deformities are found, the wire should be replaced.

Pressure Control

Pressure also must be uniform and accurately controlled across the sealing bar or wire. This is especially true of jaw-type sealers.

Pressure variations may be caused by misalignment of the sealer blade or wire or use of improper backing material. The face of the sealing jaw should be parallel to the backing pad. The preferred backing material is a high-temperature-resistant synthetic material which provides solid backing with just enough resilience to even out small pressure differences.

Most polyethylene seals are made in the 20 psi to 100 psi range. However, many heat sealers in use today were originally designed for materials requiring much higher sealing pressures. It is impossible to control them accurately at lower pressures. To produce consistently good heat seals, such equipment must be modified or replaced.

Serrated Jaws Best

Serrated jaws are preferred to smooth jaws on heat sealers as they eliminate extrusion of the film and resultant weakening of the seal. If smooth jaws cannot be avoided, pressure must be accurately controlled to prevent unnecessarily high pressures and excessive film extrusion.

With some polyethylene resins, film may stick to the jaw, whether serrated or smooth. This can be prevented by installation of a non-sticking membrane between jaw and film or application of a non-sticking jaw.

Match Machine To Use

Impulse sealers are recommended for most in-line sealing and filling operations; jaw or band-type sealers for seals that will not be subjected to immediate stress. Impulse sealing requires less heat, which is more rapidly dissipated, permitting the sealed area to cool and return to full strength sooner. Faster cooling can be achieved with water-cooled backing plates.

Many of these points apply to other kinds of sealers as well as to those mentioned. Further information is given in U.S.I.'s booklet, "Heat Seal Characteristics of Polyethylene Films and Coated Substrates". Write for your copies. And if you have specific problems, contact U.S.I. Technical Service engineers for expert assistance.

U.S.I. INDUSTRIAL CHEMICALS CO.
Division of National Distillers and Chemical Corporation
99 Park Avenue, New York 16, N. Y.
Branches in principal cities

Plastics Around the World

Continued from page 1072

The extruder, which is known to the trade as "Derex", can be used for producing tubing sheets. profiles, film, bands, cord, cable and wire covering. The extruder works with counter-current interlocking screw conveyers. The principal elements of the machine are made out of high grade steel. All gears are tempered and cut.

KUNSTSTOFFE

JANUARY 1960

Structure and properties of Metals, Glass and Plastics—pp. 3-10

A comparison of metals and plastics shows, from the point of view of the physicist, that they are more similar to one another than was thought. It may be assumed that plastics will in the future prove to be crystals with the highest degree or as liquids with the highest degree of order. Analysis of structural elements and the possible elementary process will be one of the most important tasks facing plastics research, and the final goal the completion of chemical research through structural work.

FEBRUARY 1960

Continuous Forming of Thermoplastic Sheet by a Rotational Deep Drawing Method pp. 140-142

The experience gained in conventional deep drawing processes has been used to adapt the process from a flat surface to a revolving drum. The method is continuous and the article describes results obtained so far.

KUNSTSTOFF-RUNDSCHAU

MARCH 1960

Synthesis of Furane Resins from Furfuryl Alcohol—pp. 117-121

The condensation of furfuryl alcohol with itself is so strongly exothermic that it is practically uncontrolled until the end product is formed. Water is a good solvent medium for furfuryl alcohol, but not for its condensation products. Other solvents used are ethyl acetate, methyl ethyl ketone, and acetone. Condensation products of furfuryl alcohol are synthesized with acid catalysts in aqueous solution. Specific apparatus and equipment are outlined.

TECHNICAL MEETINGS CALENDAR

17th ANTEC

Annual Technical Conference—January 24-27, 1961, Shoreham and Sheraton Park Hotels, Washington, D.C. Sponsored by the Baltimore-Washington Section. General Chairman: Dr. Gordon Kline, National Bureau of Standards, Washington, D. C.

1960 RETECS

September 8 and 9—New Horizons in Vinyls and Plastics in the Shoe Industry, Eastern New England Section, Statler-Hilton Hotel, Boston, Mass., Co-Chairman, Program, Robert Abeles, c/o Elfskin Corp., Main St., Cherry Valley, Worcester, Mass.

September 22—Plastics in Business Machines, Binghamton Section, Sheraton Inn, Binghamton, N. Y. Chairman; John E. Gwyn, c/o Consolidated Plastics, 498 Conklin Ave., Binghamton, N. Y.

October 5—Plastics vs. Corrosion, Golden Gate Section, Mark Hopkins Hotel, San Francisco, Calif. Chairman: J. W. Richardson, c/o Rohm & Haas Co., 600 California St., San Francisco 8, Calif.

November 7—Automation in Injection and Compression Molding, Ontario Section; King Edward Sheraton Hotel, Toronto. Chairman: J. M. Lees, c/o Canadian General Electric Co., 755 Division St., North Cobourg, Ontario, Canada.

November 18—Blow Molding, Newark Section, Essex House, Newark, N. J. Chairman: Robert Hoehn, Mack Molding Co., Ryerson Ave., Wayne, N. J.

1961 RETECS

April 25, Indianapolis, Ind., Central Indiana Section: **Plastics for Tooling.** Section President: Milton Brummer, 4241 Marrison Place, Indianapolis, Ind.

May 9, Detroit, Mich., Detroit Section: **Plastics in the Automotive Industry.** Section President: John D. Young, E. I. du Pont de Nemours & Co., Inc., 13000 West Seven Mile Rd., Detroit 35, Mich.

October, Niagara Falls, N. Y., Buffalo Section: **Foams.** Section President: William Dunmeyer, Carborundum Co., Buffalo Ave., Niagara Falls, N. Y.

Offers of papers for presentation at these Regional Technical Conferences are invited. Please address offers to Section Presidents, as indicated above.

SPI CONFERENCE

October 13, 14—Sixteenth Annual SPI New England Section Conference, The Society of the Plastics Industry, Inc., Wentworth-by-the-Sea, Portsmouth, N.H.

SPI EVENTS—1961

February 7, 8, 9—Sixteenth Reinforced Plastics Division Conference The Society of the Plastics Industry, Inc., Edgewater Beach Hotel, Chicago, Ill.

April 20, 21—Eighteenth Annual SPI Western Section Conference, The Society of the Plastics Industry, Inc., Hotel del Coronado, Coronado, Calif.

June 5-9—Ninth National Plastics Exposition, Sponsored by The Society of the Plastics Industry, Inc., Coliseum, New York City.

June 5-9—SPI National Conference Sponsored by The Society of the Plastics Industry, Inc., Commodore Hotel, New York City.

CONGRESS FOR MACROPLASTICS

The International Congress for Macroplastics will be held on **October 17-19, 1960,** Utrecht, Netherlands.

POLYMER SYMPOSIUM

July 27-August 1, 1961, International Symposium on Macromolecular Chemistry, Montreal, Canada. Address inquiries to: The Organizing Committee International Symposium on Macromolecular Chemistry, P.O. Box 816, Sarnia, Ontario, Canada.

SECTION NEWS

North Texas

Section Welcomes 160th Member

The North Texas Section, Society of Plastics Engineers, welcomes in their 160th member at their June 20th meeting. Here T. T. Tucker, Jr., right, president of the Section, welcomes Harry Talv, President of the Talv Mfg. Co., Heavener, Okla. at the Section meeting held at the Howard Johnson's Restaurant each month between Fort Worth and Dallas on the Turnpike. At left is Ernie Dourlet, section

secretary, while in the center is Gene Hanszen, credentials committee chairman.

Plan to attend
the 17th ANTEC
Washington, D. C.
January 24-27, 1961

Milwaukee

Blow Molding

C. H. Strong

In the final meeting of the season Mr. Vernon Hill, Director of Development, National Cleveland Corporation gave an excellent talk on blow molding, economics, and the future. He discussed the history of blow molding from its very beginning in Europe, to present day developments and discussed the growth in this country in the last two years with the introduction of linear polyethylene. He talked about the available equipment and proper selection of this equipment along with a forecast of various markets by 1965 and the pitfalls in each area.

Newark

Plastics Technology Scholarships

Allan G. Serle

The Newark Section of the Society of Plastics Engineers has announced that it will award two scholarships in plastics beginning this Fall, marking another milestone in plastics education. The spectacular growth of the plastics industry and its increasing importance and scope in our national economy make it an interesting and promising profession for many people. In awarding this scholarship, the SPE Newark Section is taking an important step in providing competent plastics technicians for the future.

These scholarships will be given to students in the Plastics Technology Certificate Program at the Newark College of Engineering, commencing in the Fall Term of 1960. These scholarships, valued at up to $225.00 per year, are awarded annually, and are subject to review and renewal through the full 3-year Certificate Program. In order to qualify for one of these scholarships, an applicant must have completed one course in the Plastics Technology Certificate Program, must be enrolled in the program at NCE, and must be in need of financial assistance. Additional information and application forms are available at the NCE Special Courses Division Office, and completed forms must be filed by August 8th.

Ontario

Annual Fishing Trip

Harold A. Shure

On July 5, 1960, seventy-six members registered at Midland, Ontario for the annual fishing trip. The Accurate Mould Co. Ltd. trophy was won by Kurt Levi of Rose Plastics, and runners-up were Jack Burnie of Monsanto and Earl Lince of Smith & Stone.

Birth of a PAC. Harry Watson, Ontario Section President, right, chats with Joseph Grenier, Iroquois Region PAC Advisor, during annual fishing trip of Ontario Section. Mr. Grenier visited the Section to counsel on the formation and operation of Professional Activity Committees (PAC).

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ABOUT MEMBERS

Ernest Csaszar, Vice President, The Newark Die Co., was named President of the Newark-New York Chapter of the Moldmaking Division of SPI.

Jerome S. Schaul recently joined the Research Staff of Lock Joint Pipe Co. He is in charge of the Plastics Section of the Research Center. He is a graduate of Columbia University, where he earned the degree in chemical engineering, in 1937.

Plastics Service Inc., manufacturing division of M. Holland Co., announces the addition to their staff of **Jack A. Peck.** Mr. Peck will be in charge of the new polyethylene and propylene division.

Mr. Shannon

Holyoke Plastics Co. has announced the appointment of **Mr. Lawrence F. Shannon** as General Sales Manager of the corporation. He is a member of the Western New England Section. The announcement was made by **George W. Martin,** President of Holyoke Plastics and also President of SPE.

Theodore W. Dwight, Jr. heads up sales for Crawford & Russell, Inc., Cleveland, Ohio, branch.

Don B. Pettry joins Flexible Products Co. as Sales Manager. He was formerly a sales engineer for Firestone Plastics Co. in Pottstown, Pa.

Philip C. Greene, former Sales Manager of Davis-Standard, has been named Division Manager of the company. Also within the sales department, **Dennis Deveau** was appointed sales product manager for Wire & Cable Machinery.

Leonard Simon is now president of the newly-formed Amity Plastics, Inc., injection molders. Mr. Simon was formerly plant manager for Reliance Plastics.

Bert S. Taylor joins the Business and Defense Services Administration as Assistant Director for Mobilization Planning, Chemical and Rubber Division. Mr. Taylor is director of marketing and purchasing for the Chemicals and Plastics Div. of Food Machinery and Chemical Corp., and goes to BDSA under an arrangement by which industry makes the services of key executives available for temporary assignment—usually six months—without compensation from the government.

Mr. Usab

Martin Usab, was elected president of Dynatech Plastics, Inc., at a special meeting of the Dynatech Board of Directors. He resigned his post as vice president of Rexall Drug and Chemical Co., Los Angeles, to accept the Dynatech position.

Herbert O. Corbett has been promoted to chief extrusion technologist for The Kordite Co. He will be responsible for invention, development, and consultation in all areas of plastics extrusion used by Kordite. Mr. Corbett is a member of the board of directors of the Rochester Section of SPE.

Ernest R. Summers has been appointed Plant Manager for Norton Laboratories, Lockport, N. Y. Summers had served as manager of product engineering, and prior to that was a product engineer with Norton Laboratories.

Williar R. Kidder, Vice President of Wilson & Geo. Meyer & Co., Western representatives for plastics, chemicals, and synthetic fibers marketed by Eastman Chemical Products, Inc., has been transferred to the company's San Francisco headquarters. Mr. Kidder had been in the firm's Southwest Div. in Los Angeles.

Mr. Kidder

Kent Doolittle has been named general manager of the Western Operation of CTL Div. of Studebaker-Packard Corp.

Ken Cressy will supervise product development of building trades materials and electrical products for Furane Plastics.

Monsanto Chemical Company assigns **Lee T. Johnson** as paper chemicals specialist in the up-state New York territory.

Stewart Helliwell, Midwest Regional Manager of F. J. Stokes Corp., Philadelphia, has been placed in charge of all Press Division applications. The Division's products include a complete line of automatic and semi-automatic compression and transfer plastics molding presses.

Andrew A. Dukert has joined the recently-organized Research Products Development Dept. of Pennsalt Chemicals Corp. as a plastics application engineer.

Jim Redman has been appointed Sales Representative covering the 11 Western States for Nypel Corp., producers of nylon molding pellets.

H. D. Cooper, formerly polyethylene product Manager, Koppers Co., has been named Assistant Sales Manager of the company's Plastics Division. Mr. Cooper is a graduate of Pennsylvania State University.

Mr. Cooper

William E. Decker, Technical Director of The Crystal Essence Corp. has announced the appointment of **Mr. Charles S. Langdon** as Director of Sales

Harry A. Russell was promoted to Executive Vice President of the Pantasote Company of Passaic, New Jersey.

Deaths

John L. Mack, Jr. Vice President of John Mack & Son Molded Products, Inc. died on May 17, 1960. He had been employed in the plastics industry for 25 years.

Employment & Service Guide

POSITIONS OPEN

PLASTICS DEVELOPMENT ENGINEER

We have a NEW position in our NEW Products Development Dept. for an engineer to work on fabrication techniques for NEW thermoplastics. Location: NEW $6 million research center in suburban Maryland, near Washington, D.C. B.S. minimum, 3-10 years broad experience in fabrication of plastics, especially extrusion. Replies confidential. Send resume to Dr. David M. Clark, W. R. Grace & Co., Research Division, Clarksville, Md.

EXTRUSION TECHNICIAN AND PROJECT ENGINEER

Should have experience in extrusion of various types and shapes of engineering plastics, including nylon, polyethylene, etc. New England location. Excellent opportunity. Apply Box 7665, SPE JOURNAL, 65 Prospect Street, Stamford, Conn.

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A. C. Martinelli-Rogers Plastic Corporation needs several production supervisors and key men experienced in automatic molding for our expanded facilities. We offer good salary, bonus plan, fringe benefits, as well as a good future to the right men. Send references and resume. All inquiries strictly confidential. Write direct to:

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General Employment Manager

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Nine years' experience Rubber and Plastics Technology, in following phases: Research and Development, Market Surveys, Sales Promotion, Production, Technical Sales Service. Knowledge of natural and synthetic lattices and elastomers, vinyls, polyesters, urethanes, epoxies. Seeking heavy responsibility in rubber and plastics (or related) industry. Reply Box 7800 SPE JOURNAL, 65 Prospect St., Stamford, Conn.

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Allied Chemical Corp.—Plastics & Coal Chemicals Div. ..... Cover 2
Allied Chemical Corp.—National Aniline Div. 1065
American Cyanamid Co.—Plastics & Resins Div. 999
Argus Chemical Corp. 1027, 1028, 1029, 1030
Cadet Chemical Corp. 1022
Celanese Corp. of America—Chemicals 1023
Detroit Mold Engineering 1058
Dow Chemical Co.—Coatings; Molding Materials 1013, 1057
Emery Industries, Inc. 1063
Enjay Chemical Co., Inc.—Plastics 1002
General Dyestuff Corp. ..... Cover 4
Gering Plastics, Inc., Div. Studebaker-Packard Corp. ..... Cover 3
W. R. Grace & Co., Polymer Chemicals Div. 1000, 1001
Harchem Div., Wallace & Tiernan, Inc. 1068
Improved Machinery, Inc. 1012
Injection Molders Supply Co. 1020
Lucidol Div., Wallace & Tiernan, Inc. 1069
The Mearl Corp. 1010
Monsanto Chemical Co.—Plastics 1006, 1007, 1038
National Aniline Div., Allied Chemical Corp. 1065
National Distillers & Chemical Corp., U.S. Industrial Chemicals Co. Div. 1071, 1072
National Lead Co. 1004
National Rubber Machinery Co. 1014
Package Machinery Co.—Reed-Prentice Sales Div. 1003
Phillips Chemical Co. 996
Plastics and Coal Chemicals Div., Allied Chemical Corp. ..... Cover 2
Reed-Prentice Sales Div., Package Machinery Co. 1003
Reichhold Chemicals, Inc.—Plastics 1011
John Royle & Sons 998
Spencer Chemical Co. 1008, 1061
Union Carbide Plastics Co., Div. Union Carbide Corp. 1036, 1037
U. S. Industrial Chemicals Co., Div. of National Distillers & Chemical Corp. 1071, 1072
Van Dorn Iron Works 995
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Permanent Yellow		■	■	■
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Permagen Orange		■	■	■
Permanent Red	■		■	
BON Reds				
Permagen Red		■	■	■
Dioxazine				
Permanent Violet	■	■	■	■
Naphthols				
Helio® Red		■	■	
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Parachlor Red				
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Heliogen® Blue	■	■	■	■
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